COMPTES RENDUS

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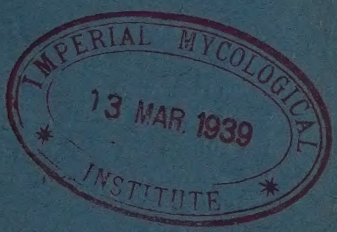
DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1938



VOLUME XXI

№ 8

ÉDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
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15 Décembre

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(DOKLADY)

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NOUVELLE SÉRIE

6-me année

Paraissant tous les dix jours

1938

VOLUME XXI, № 8

TABLE DES MATIÈRES

Pages

PHYSIQUE

V. Prujinina-Granovskaja. Galvano-Magnetic Phenomena in a Dielectric Material (Mica) 367

PHYSIQUE DU GLOBE

A. B. Melikian. Sur une méthode de détermination rapide des variations de l'accélération de la pesanteur 371

BIOPHYSIQUE

S. I. Wawilow, Member of the Academy. Sensitivity of the Retina to the Ultra-Violet Spectrum 373

CHIMIE

V. O. Lukashevich. The Preparation of Mixed Azoxycompounds by the Action of Nitrosocompounds on β-Arylhydroxylamines 376

V. P. Radiščev. On Some General Principles which Characterize Multicomponent Mutual Systems 380

V. P. Radiščev. On Some Physico-Chemical Properties of Multicomponent Mutual Systems 385

V. P. Radiščev. On the Topological Structure of the Stable Complexes of Multicomponent Mutual Systems and the Classification of Their Diagrams 389

CHIMIE PHYSIQUE

K. F. Zhigatch, P. A. Rehbinder, Corresponding Member of the Academy, and **G. G. Edelman.** Influence of Surface-Active Substances on Structure Formation in Gelatin Sols 392

STRATIGRAPHIE

N. B. Vassoevich. Neocome and Jurassic Deposits in the Lagich Mountains of Azerbaidjan 396

N. B. Vassoevich. On the Presence of Albian Deposits in North-Eastern Azerbaidjan 400

MORPHOLOGIE EXPÉRIMENTALE

A. Rumyantzew. The Action of an Excess of Na, K, Ca-Chlorides on the Cytoplasmic Structures of Embryonic Tissue 405

PALÉONTOLOGIE

A. G. Eberzin. Horizon with *Congeria subrhomboidea* Andrus. in the Kuban Province 409

Rédacteur en chef A. Fersman. Rédacteur S. Bernstein.

En composition 10/XII 1938. En impression 17/I 1939. Nombre de feuilles d'impression 3. Nombre de caractères par feuille d'impression 65 000. Pages 365—412. Format du papier 72×110 cm. Tirage 1 000. Glavlit A 3304. Numéro d'édition 2057. Numéro typographique 1900.

Imprimerie № 16. Moscou. Trekhproudnij péréoulok, 9.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

PHYSICS

GALVANO-MAGNETIC PHENOMENA IN A DIELECTRIC MATERIAL (MICA)

By V. PRUJININA-GRANOVSKAJA

(Communicated by A. F. Joffe, Member of the Academy, 25. X. 1938)

1. It has been found that electronic conductivity appears in dielectrics in a strong electric field (1). The existence of galvano-magnetic effects, well-known with metals and semi-conductors, as well as with insulating crystals in photoconductivity, is connected with the availability of this electronic conductivity (2). The present work had as its purpose to disclose these effects in a dielectric (mica) under the conditions of the existence of dark electronic conductivity.

2. The transverse galvano-magnetic effect—or the Hall-effect—was determined according to the compensation scheme with an electrometer, or under stated conditions, with the help of a galvanometer. The specimen was made up of two plates each 8—12 μ thick. A small rectangular current bearing electron was applied to one of the surfaces of the first plate. The other surface was provided with two Hall-electrodes in the shape of narrow and extremely thin platinum bands. The second plate had but a single rectangular electrode serving as the second electrode for the supply of current. The electrodes were applied by cathode pulverization. The plates were folded in such a way as to make the Hall-electrodes lie inside. The specimen was mounted on a polished quartz plate and was then placed into a furnace located between the poles of an electromagnet.

It being impossible, under the conditions of a dielectric, to locate the Hall-electrodes exactly over the equipotential surface, there arose the need of compensating for the potential difference (the voltage of the compensation amounted to 20—80 volts). In consequence of this circumstance the Hall-effect could be superimposed by a longitudinal effect, i. e. the effect of the variation of resistance with the switching on of the magnetic field.

The Hall-effect with mica was observed in fields of the order of 10^5 V/cm at a temperature of $\sim 350°$ C. It was noticed simultaneously with the longitudinal effect and became manifest in a considerable asymmetry of the longitudinal effect which, as is well known, does not change its sign with a change in the sign of the magnetic field. As to its magnitude, the Hall-effect was found to be of the order of 10^{-3}—10^{-4} volts.

The magnitude of the effect permitted of conducting measurements only with the help of a galvanometer. The possibility of making use of the latter appears under the conditions in which electrical conductivity reaches the order of $10^{-8}\Omega^{-1}$. These conditions for mica are available at the temperature

of ~350°C. Owing to this, the study of the dependence of the Hall-effect upon field and temperature would have required the performance of experiments within the high temperature range. But this is prevented by ion-conductivity, which can no longer be dismissed as of little consequence under these conditions (particularly in the region of weaker fields)*. Therefore, dependence upon field and temperature could be investigated only for the longitudinal effect.

3. The method of determination of the longitudinal galvano-magnetic effect consisted in the following: a mica crystal was mounted on a quartz plate and placed between the poles of an electromagnet. A constant voltage of 100—1000 volts was imposed upon the crystal, as well as upon resistance r, connected to the crystal in series. On switching on the magnetic field the resistance of the crystal increased, in result of which the distribution of tensions between it and the constant resistance r underwent a change. This change was recorded either by an electrometer or galvanometer according to the bridge scheme depending on the resistance of the specimen determined by temperature. Resistance r, just as the other resistances incorporated in the bridge scheme, composed a box of resistances of several megohms. The magnitude of the effect characterized by ratio $\frac{\Delta R}{R}$, in which R is the resistance of the crystal without magnetic field and Δ is increment of resistance upon the switching on the magnetic field, was determined according to the formula:

$$\frac{\Delta R}{R} = \frac{V}{V - V'} \frac{\Delta V}{V' - \Delta V}.$$

Here V is the potential of the common point of the battery and the crystal, i. e. voltage in circuit $R + r$ (one pole of the battery and one end of resistance r were earthed); V' is the potential of the common point of the crystal and resistance r; ΔV is change in potential at the same point upon switching on the magnetic field.

4. The longitudinal galvano-magnetic effect in mica was detected in fields of the order of 10^5 V/cm and within the temperature range of 125—355° C. It varied inversely with the magnetic field and did not show any lag relatively to the field. The dependence of this effect upon the three following factors was considered: a) intensity of magnetic field, b) temperature, c) tensity of electric field.

a) The dependence of the longitudinal effect upon the intensity of the magnetic field within the range of 2000—8500 oersted was found to satisfy the relation $\frac{\Delta R}{R} = BH^2$, where B is constant. This dependence, holding also for metals, is fulfilled with mica throughout the whole range of temperatures in which measurements of the effect were accomplished (125—355°C).

The respective data for the case: $t = 303°C$, $E = 6.89 \cdot 10^5$ V/cm are given in Table 1.

Table 1

H oersted	$\frac{\Delta R}{R}$	$\frac{\Delta R}{R} / H^2$
3690	$1.36 \cdot 10^{-4}$	$1.00 \cdot 10^{-11}$
4670	$2.075 \cdot 10^{-4}$	$0.95 \cdot 10^{-11}$
5770	$3.38 \cdot 10^{-4}$	$1.01 \cdot 10^{-11}$
7290	$5.16 \cdot 10^{-4}$	$0.97 \cdot 10^{-11}$
8020	$6.62 \cdot 10^{-4}$	$1.03 \cdot 10^{-11}$
8520	$8.50 \cdot 10^{-4}$	$1.17 \cdot 10^{-11}$

*Let us note, by the way, that the accomplishing of these experiments at a temperature ~350° C is very difficult.

The behaviour of the curve in stronger magnetic fields was not examined.

b) The typical dependence of $\frac{\Delta R}{R}$ upon temperature with constant magnetic ($H = 8100$ erg.) and electric ($E = 7.57 \cdot 10^5$ V/cm) fields is represented in Fig. 1. The break of the curve corresponds to a temperature of about 285°C. Similar curves were obtained also with other values of the intensity of the electric field.

c) The dependence of $\frac{\Delta R}{R}$ upon the intensity of the electric field with constant magnetic field and constant temperature is represented in Fig. 2.

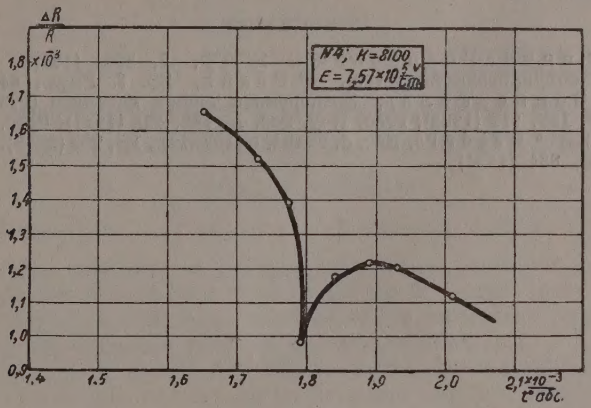

Fig. 1. Dependence of $\frac{\Delta R}{R}$ on the temperature.

We see that at first $\frac{\Delta R}{R}$ decreases rapidly, yet, a further increase of the field involves a slower growth of the effect.

The intensity of the field corresponding to the minimum of the curve depends upon temperature and in proportion with the rise of the latter becomes shifted in the direction of weaker fields (Table 2).

Table 2

t°,C	E_{min} (V/cm)
126	$>10 \cdot 10^5$
270	$4.75 \cdot 10^5$
305	$4.25 \cdot 10^5$
355	$3.15 \cdot 10^5$

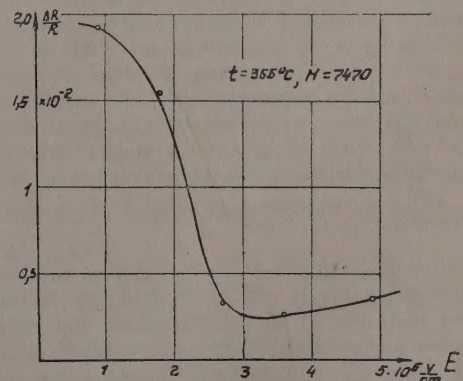

Fig. 2. Dependence of longitudinal galvano-magnetic effect on the stress of the electric field.

5. According to the theory of galvano-magnetic phenomena in metals ([3],[4]), the magnitude of the longitudinal effect is greater for the case of fixed electrons than for that of free electrons. The effect for the latter in the first approximation is equal to zero ([4]). In the light of quantum theories of the isolating lattice ([5],[6],[7]) we may consider that in crystalline dielectrics the same phenomenon will take place. Accordingly, the rather

greater magnitude of the longitudinal effect with mica (10^{-2}—10^{-3}) alongside of the small magnitude of the Hall-effect permit to draw the conclusion that in mica conductivity is brought about by fixed electrons.

The experimental curves of Fig. 1 and 2 afford a certain possibility of drawing conclusions relating to the change in concentration and mobility of conductivity-electrons occurring with change in field and temperature. These results will be published additionally.

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Received
26. X. 1938.

REFERENCES

[1] Пружинина-Грановская, ЖЭТФ, **7**, 506 (1937). [2] Иоффе, Электронные полупроводники (1933). [3] Frank, ZS. f. Phys., **64**, 650 (1930). [4] Бете и Зоммерфельд, Электронная теория металлов (1938). [5] Wilson, Nature, **130**, 913 (1932); Proc. Roy. Soc. A, **133**, 458 (1931); Proc. Roy. Soc. A, **134**, 277 (1931). [6] Peierls, Erg. d. exakt. Naturwiss., XI, 265 (1932). [7] Bloch, Phys. ZS., **32**, 881 (1931).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

PHYSIQUE DU GLOBE

SUR UNE MÉTHODE DE DÉTERMINATION RAPIDE DES VARIATIONS DE L'ACCÉLÉRATION DE LA PESANTEUR

Par A. B. MELIKIAN

(Présenté par S. I. Wawilow, de l'Académie, le 29. X. 1938)

Les mesures relatives de l'accélération de la pesanteur au moyen des pendules ont des défauts dont le principal est la longue durée des mesures. En URSS, ainsi qu'à l'étranger, on effectue des recherches pour obtenir des méthodes et des appareils pour les mesures rapides de g.

Au commencement de l'année 1938 nous avons abordé l'étude de la méthode qui, étant dynamique en fait, ne se distingue pas des méthodes statiques connues au point de vue de rapidité de détermination des variations de la valeur de g. L'idée de cette méthode, proposée encore en 1935 par L. I. Mandelstam et N. D. Papalexy, a été présentée au conseil de l'Institut physique de l'Académie des Sciences en automne de 1937. Comme dans le No 6 des C. R. (du 8 Août 1938) a été publié l'article de M. G. Bertrand exposant une méthode de mesurages de g basée sur les mêmes idées, nous avons trouvé utile de publier les résultats déjà obtenus par nous.

L'idée de la méthode donnée de détermination rapide des variations de g est basée sur le rapport de la fréquence ν de la corde vibrante à sa tension P.

Si la tension de la corde est conditionnée par la masse M suspendue à cette corde, de sorte que $P=Mg$, on peut d'après les variations de ν, en se servant des relations connues (la formule de Seebeck, par exemple) juger de la variation de g. La sensibilité de la méthode peut être augmentée d'une façon considérable par la compensation de la grande partie de la force Mg (par exemple, à l'aide des ressorts), de sorte que ce n'est que la force $Mg—C$ qui agira sur la corde, C étant une force constante dans les conditions d'une expérience. Dans ce cas la sensibilité de la méthode augmente en $\frac{Mg}{Mg—C}$ fois environ.

Les expériences décrites dans le présent article ont été destinées à la détermination préliminaire de la sensibilité de cette méthode. Il fallait savoir si la vibration de la corde est stable, car la sensibilité de la méthode est avant tout fonction de cette stabilité. Nous avons utilisé une corde à excitation propre. La corde était excitée dans le second harmonique. Les oscillations dans la partie électrique du schéma de la corde à excitation propre agissaient sur un système relaxé et le synchronisaient, le rapport des fréquences étant 1 : 1. Des oscillations du système relaxé synchronisé se distinguait le 22 harmonique avec la fréquence $\sim$ 24 000 Hz. On comparait ces oscillations aux autres, ayant la fréquence voisine et stable; on prenait le

quatrième harmonique d'un oscillateur de piezo-quartz, dont la fréquence fondamentale est $\sim$ 96 200 Hz. Les battements entre les fréquences comparées (de l'ordre de 40—60 Hz) agissaient sur un compteur de fréquences à langues, nous servant de l'indicateur de stabilité. Les langues voisines du compteur se distinguaient les unes des autres de 0.5 période. Les expériences ont montré que dans notre installation les variations de fréquences, pendant plusieurs heures, peuvent ne pas dépasser $1—1.5 \cdot 10^{-5}$. On a trouvé aussi que la dépendance de la fréquence de la corde à excitation propre des tensions de la partie électrique du schéma est faible. Par exemple, pour les petites amplitudes des vibrations de la corde la variation de la tension d'anode de 1% ne produisait que la variation de fréquence de la corde de l'ordre $1 \cdot 10^{-6}$. Par conséquent, dans les conditions de laboratoire, on peut distinguer la variation du poids (et par conséquent de la force tendant la corde) moindre que $1 \cdot 10^{-4}$ partie.

Il faut noter qu'au cours de ces expériences n'ont pas été prises les mesures spéciales pour neutraliser l'influence déstabilisante des variations de température et des propriétés physico-mécaniques du régime électrique du système.

Les résultats obtenus donnent à croire qu'en tenant compte et en éliminant l'influence des facteurs déstabilisants indiqués, de même qu'en effectuant la compensation d'une partie de la force Mg, il sera possible d'augmenter considérablement la sensibilité de cette méthode.

Les recherches dans ce sens continuent.

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Académie des Sciences de l'URSS.

Manuscrit reçu
le 29. X. 1938.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

BIOPHYSICS

SENSITIVITY OF THE RETINA TO THE ULTRA-VIOLET SPECTRUM

By S. I. WAWILOW, Member of the Academy

§ 1. Basing upon the conception of the quantum-structure of light and the fact of the enormous sensitivity of the eye adapted to obscurity, E. M. Brumberg and I have developed a method which by means of quantitative measurements of quantum-fluctuations of the light flux (1) permits to determine the number of the photons, producing the optical sensation at the threshold of vision. The important advantage of this method consists in that it enables the physiologist and optician to investigate the sensitivity of the retina of a normal, live eye, no matter what is the absorption of the eye mediums the light encounters on its way to the retina. By using this method we have determined the spectral sensitivity of the retina within the range of 6600 to 3400 Å for one observer and of 6000 to 4000 for another (2). In Table 1 are given the numbers of the photons n_0, which correspond to the threshold for varying wave lengths for two observers. The measurements refer to the region of the retina 10° from the fovea. The same data are graphically represented in Fig. 1, where the relative sensitivity of the eye, equalized for both observers within the region 5100 Å, is plotted along the axis of the ordinates.

Table 1

λ (mμ)	660	640	620	600	580	560	540	520	515	510	505	500	480	460	450	440	420	400	380	360	340
n_0 (I)	280	200	97	50	39	22	12	10.6	9.7	8.4	8.0	8.0	12	18	—	46	93	23	7	18	42
n_0 (II)	—	—	—	200	—	—	—	46	—	29	—	32	50	—	87	—	—	72	—	—	—

The solid line in Fig. 1 represents the curve of the crepuscular sensitivity after Hecht. Within the visible part of the spectrum the sensitivity determined from fluctuations coincides fairly well with this curve, in spite of the absolute values of sensitivity for both observers being one four times that of the other. Within the ultra-violet spectrum, however, a sharp discrepancy is observed. In contradistinction to the well-known fact of extreme reduction of the eye sensitivity to the ultra-violet spectrum, the fluctuational observations lead us to the conclusion as to the existence in this region of a steep rise of the retina sensitivity. According to one of the observers, who had collected abundant and repeatedly reoccurring data, in the neighbourhood of 3800 Å there exists a second steep sensitivity maximum, the value of which nearly attains that observed within the blue-green part of the spectrum.

§ 2. As to its qualitative aspect, this rather unexpected result should be first of all compared with the familiar fact of a very strong light absorption within the eye mediums, especially within the crystalline lens, in the ultra-violet spectrum, beginning at 4000 Å. The poor sensitivity of the eye as a whole to ultra-violet rays should be referred to the retina being reached by an insignificant portion of the incident light energy. The sharp increase of the eye sensitivity to ultra-violet rays, long ago observed in patients who had been subjected to the extraction of the crystalline lens, qualitatively agrees with the results of fluctuational observations (3).

Recently there were published most curious observations by Gaydon (4), the comparison of which with the data obtained by the fluctuation method constitutes the object of the present communication.

Owing to an explosion that had occurred in his laboratory, Gaydon lost his right eye, and the crystalline lens in the left eye was removed by

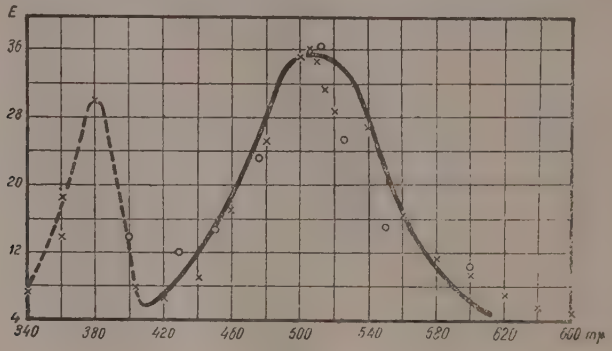

Fig. 1.

operation. With the help of this operated eye, armed with glass or quartz spectacles, Gaydon is carrying on his spectrographic work. The sensitivity of Gaydon's eye to the ultra-violet region of the spectrum has extraordinarily increased, which enables him to make visual observations in the spectrum at least up to 3000 Å: «Some idea of my abnormal sensitivity may be gained from the fact that I find it easier to focus the slit width of a 20-ft concave grating spectrograph by observing second-order 3400 Å than by using the first-order 6800 Å».

For sake of comparison with Table 1 and Fig. 1 we are giving here Table 2 from Gaydon's article, this table containing qualitative observations made by him through a quartz ocular in the iron-spectrum.

When comparing Table 2 with Table 1 and Fig. 1, it seems as if one was reading a quantitative verbal description of the data contained in § 1, including the existence of a sharp maximum at 3800 Å. Taking into account the distribution of energy in the iron-spectrum, as well as the fact that Gaydon's observations have been effected at relatively high intensities, while the data of § 1 refer to observations made at the threshold of vision, nevertheless one can but state the coincidence of the results of fluctuation measurements with those of Gaydon's observations.

It should be noted, moreover, that according to his own statement, Gaydon's eye sensitivity within the region 3650 Å is about 1000 times that of a normal eye, i. e. the maximum in the ultra-violet spectrum is of the same order of magnitude as in the visible part of the spectrum, which also agrees with the fluctuation measurements.

Table 2.

Wave lengths (Å)	Remarks
7000 to 4600	Normal; intensity maximum in the green
4500	Blue
4400 to 4300	Blue-violet
4200 to 3900	Violet, but much stronger than observed previously
3800 to 3700	Very strong whitish-violet. The spectrum between 3850 and 3800 Å is very intense and is almost comparable in apparent brightness with the green maximum, the light being unbearably bright, if the slit is opened to a width of about 0.1 mm. This intensity is probably largely accounted for by the intensity of the iron-spectrum in this region
3650	Strong whitish blue-violet
3600 to 3150	Strong blue
3100	Blue. There is some indication that the 3100 Å iron triplet is a slightly more violet shade of blue, but this may be only a contrast effect due to the strong blue sensation produced by the neighbouring light
3091	Only just visible with normal slit width
3083	Invisible

State Optical Institute.
Leningrad.

Received
11. XI. 1938.

REFERENCES

[1] E. Brumberg and S. Wawilow, Bull. Acad. Sci. URSS, 919 (1938). [2] S. I. Wawilow, Bull. Acad. Sci. URSS, série phys., No 1—2, 163 (1938). [3] J. Widmark, Mitt. aus Augenkl. zu Stockholm, **31** (1898). [4] A. G. Gaydon, Proc. of the Phys. Soc., **50**, 714 (1938).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

CHEMISTRY

THE PREPARATION OF MIXED AZOXYCOMPOUNDS BY THE ACTION OF NITROSOCOMPOUNDS ON β-ARYLHYDROXYLAMINES (1)

By V. O. LUKASHEVICH

(Communicated by M. A. Iljinsky, Honorary Member of the Academy, 10. X. 1938)

According to Bamberger (2) the interaction of nitrosocompounds and β-arylhydroxylamines having dissimilar radicals leads exclusively to the formation of symmetrical azoxycompounds (1)*:

$$2R_1NO + 2R_2NH \cdot OH \rightarrow R_1N(O) = NR_1 + R_2N(O) = NR_2 + 2H_2O. \qquad (1)$$

Simultaneously with the azoxycoupling reaction there undoubtedly takes place an oxydation-reduction process which in the case examined above may be represented by the following scheme:

$$R_1NO + R_2NH \cdot OH \rightleftarrows R_2NO + R_1NH \cdot OH. \qquad (2)$$

Thus, the reason for the formation in this case of symmetrical azoxycompounds is obvious.

It remains, however, incomprehensible what prevents the formation of mixed azoxycompounds, the more so, as mixtures of two different nitrocompounds when subjected to electrolytical reduction yield mixed azocompounds (6). The latter, if one follows the generally accepted explanation, can be obtained only by way of the corresponding azoxycompounds. Their formation should take place as a result of the oxydation of hydrazocompounds, i. e. of the products of the direct reduction of azoxycompounds by means of nitrocompounds remaining in the reaction mixture.

All these considerations prompted us to verify the correctness of the statement advanced by Bamberger.

At first we tried to obtain the monocarboxylic acids of azoxycompounds, which are very easy to identify. These compounds were obtained by the action of the simplest nitrosocompounds upon the 3 isomeric hydroxyla-

* Later Bamberger described as an exception from this rule the formation of *p*-oxyazoxybenzene by the condensation of *p*-nitrosophenol with phenylhydroxylamine (3). In the literature we have found another case when a small amount of a very impure azoxybenzene-2-carboxylic acid was obtained from *o*-nitrosobenzoic acid and phenylhydroxylamine (4). Recently Müller and Kreutzmann (5) have tried, though without result, to obtain a mixed azoxycompound from *o*-chlorophenylhydroxylamine and *o*-bromonitrosobenzene.

mine-benzoic acids. In all cases together with symmetrical azoxycompounds mixed ones were obtained in large quantities (sometimes 2 isomers).

Then we turned over to the examples described by Bamberger and studied the action of nitrosobenzene on *p*-chlorophenylhydroxylamine and *p*-bromophenylhydroxylamine. Again considerable amounts of mixed azoxycompounds were isolated, and in the second case 2 isomers were obtained, corresponding to the α-β forms of Angeli (7).

Thus, the interaction of nitrosocompounds and β-arylhydroxylamines having dissimilar radicals leads invariably to the formation not only of symmetrical azoxycompounds, but also of mixed ones. Their relative yields depend, apparently, on the rates of the oxydation-reduction processes, according to equation (2), as well as on the rates of the azoxycoupling of different nitrosocompounds and β-arylhydroxylamines.

By contrasting the regularity found by us with the statement of Bamberger, we consider at the same time that the vagueness in the question of the formation of azoxy- and azocompounds which was mentioned above has been removed.

Experimental. The 3 isomeric hydroxylamine-benzoic acids were prepared by the reduction with zinc dust and ammonium chloride in the cold of the ammonium salts of the nitrobenzoic acids. The yield of the *m*-isomer was 70%, the yield of the other two—50—60%. They were 96—98% pure.

m-nitrobenzoic acid. We have substituted the rather unsatisfactory method of Alway (8) with the oxydation of the hydroxylamine itself dissolved in alcohol, with a water solution of ferric chlorid.

Mixed azoxycompounds. All the mixed azoxycompounds were well crystallizing bodies of a light yellow colour. For identification they were converted into azocompounds by reductoin in water-alcohol solution with sodium amalgam with a subsequent oxydation by means of mercuric oxide. In turn in some cases the azocompounds were converted in the initial azoxycompounds using the oxydation with hydrogen peroxide in acetic acid. First, there are described azoxycompounds that were obtained by the action of *m*-hydroxylamine-benzoic acid on the suitable nitrosocompounds. For this purpose solutions of 0.02 mol of *m*-hydroxylamine in 30 cm³ of alcohol were heated up to 30—35° and then mixed with solutions of nitrosocompounds in 20 cm³ of alcohol. The mixture warmed up to 45—50° and 1—2 minutes later the odour of the nitrosocompounds disappeared. The further treatment of the reaction mixture which was alike in the case of all these compounds is illustrated by the following example.

Azoxybenzene-3-carboxylic acid. The reaction mixture was filtrated without cooling and the precipitate (I) was washed with 20 cm³ of alcohol. The filtrate was evaporated at diminished pressure up to $^1/_3$ and diluted with water containing an excess of ammonium hydroxide. The azoxybenzene was extracted with a mixture of benzene and ether; after the evaporation of the solvents 0.94 g of azoxybenzene were obtained. The water solution was heated, acidified, the precipitate was separated, dried, ground and treated with boiling toluene. 0.22 g of *m*-azoxybenzene-dicarboxylic acid did not dissolve. After cooling the toluene solution, 1.68 g of almost pure azoxybenzene-3-carboxylic acid having a m. p. 183—184° were obtained, and after the evaporation of the toluene 0.11 g more of an impure product were isolated. (I) was ground in a mortar with 20 cm³ of alcohol and treated with hot toluene. After the distillation of the alcohol 1.40 g of *m*-azoxybenzene-dicarboxylic acid having a m. p. 310—320° were separated. 0.47 g of absolutely pure azoxybenzene-3-carboxylic acid were obtained from the filtrate. The azoxybenzene-3-carboxylic acid crystallizes from alcohol and benzene in spindle-like needles having a m. p. 184—185°. In a similar way the azoxy-

benzene-3-carboxylic acid was obtained by the action of *m*-nitrobenzoic acid on phenylhydroxylamine.

The azobenzene-3-carboxylic acid ([9]) crystallizes from alcohol and benzene in prisms having a m. p. 171—172°.

2′-Methylazoxybenzene-3-carboxylic acid. 1.66 g of the dicarboxylic acid, 1.25 g of *o*-azoxytoluene and 2.24 g of mixed azoxy-compounds were obtained. After treating the latter with ammonium hydroxide, 1.11 g of a pure substance were obtained in the form of the ammonium salt, having a m. p. 176 –176.5°. The free acid crystallizes from alcohol in long fine prisms. Through crystallization of the remaining mixture of isomers from benzene and ligroin, 0.26 g of the second isomer, which crystallizes from ligroin in needles, forming druses and having a m. p. 142—143°, were isolated.

2′-Methylazobenzene-3-carboxylic acid from water alcohol solution and acetic acid crystallizes in prisms, mostly curved and twisted in the shape of bands; m. p. 162—163°.

3′-Methylazoxybenzene-3-carboxylic acid (2.08 g) was isolated together with 1.71 g of the dicarboxylic acid and 1.08 g of *m*-azoxytoluene. This acid crystallizes from alcohol and benzene in very small needles, forming very compact druses, m. p. 188—189°.

3′-Methylazobenzene-3-carboxylic acid crystallizes from alcohol or benzene in prisms, m. p. 166.5°—167.5°. It was obtained in a good yield by the interaction of *m*-aminobenzoic acid and *m*-nitrosotoluene in glacial acetic acid in the cold for 40 hours.

4′-Methylazoxybenzene-3-carboxylic acid (2.23 g) was obtained together with 1.03 g of *p*-azoxytoluene and 1.53 g of the dicarboxylic acid. It crystallizes from alcohol, toluene and acetic acid in fine curved prisms; very small crystals resemble coils. M. p. 209—210°.

4′-Methylazobenzene-3-carboxylic acid besides the usual method was obtained in a good yield by heating a solution of *m*-aminobenzoic acid and *p*-nitrosotoluene on a water bath. Lustrous orange hexagonal plates, m. p. 209.5—210°. Alway ([10]) and Löb ([11]) for a substance obtained by a different method give a m. p. 192°.

4′-Chloroazoxybenzene-3-carboxylic acid. 2.3 g of this acid were isolated. From alcohol and toluene it crystallizes in long prisms, m. p. 258—259°. Its salts with alkali metals are poorly soluble in water.

4′-Chloroazobenzene-3-carboxylic acid—long prisms from alcohol and toluene; m. p. 244.5—245.5°.

Azoxybenzene-2-carboxylic acid. Solutions of 0.04 mol of *o*-hydroxylamine-benzoic acid and nitrosobenzene, each in 20 cm³ of alcohol, were heated to 50—60°, mixed together and again heated for 15—20 minutes. 1.68 g of azoxybenzene, 2.39 g of *o*-azoxybenzene-dicarboxylic acid and 4.58 g of «crude» azoxybenzene-2-carboxylic acid were isolated. The latter could be easily separated from the dicarboxylic acid by hot benzene.

After a single crystallization from dilute acetic acid it melted at 126—127°. From dilute acetic acid or ligroin it crystallizes in rhombic plates having a m. p. 127—128°. Freundler gives a m. p. 118° ([12]) and 110—111° ([13]). Reissert and Lemmer ([14]) give a m. p. 105—106°. By the usual method the azoxy-compound was converted into the already known azobenzene-2-carboxylic acid, which crystallizes from dilute acetic acid and ligroin in needles or hexagonal plates having a m. p. 92.5—93.5°.

2′-Methylazoxybenzene-2-carboxylic acid (5.62 g) was obtained as described above, when nitrosobenzene was substituted by *o*-nitrosotoluene. 1.7 g of the dicarboxylic acid and 1.38 g of *o*-azoxytoluene

were also found. From alcohol and acetic acid the acid crystallizes in prisms, m. p. 150—152°.

2′-Methylazobenzene-2-carboxylic acid. Beautiful, very fine prisms, coloured red-orange, from dilute acetic acid and alcohol; m. p. 138.5—139.5°.

Azoxybenzene-4-carboxylic acid, corresponding to the β-form of Angeli (7). 2.1 g of this acid were obtained by the action of nitrosobenzene on *p*-hydroxylamine-benzoic acid, similarly with the azoxybenzene-3-carboxylic acid.

4-Chloroazoxybenzene. 0.03 mol of nitrosobenzene were added rapidly to 0.03 mol of *p*-chlorophenylhydroxylamine in 100 cm³ of alcohol at 25°. In 1—1$\frac{1}{2}$ minutes the reaction was completed. The reaction mixture was heated until the precipitate dissolved and after cooling 2.08 g of yellow crystals, m. p. 125—144°, were isolated (I). The filtrate was cooled with a freezing mixture; 0.78 g were isolated melting at 55—75° (II). After the evaporation of the second filtrate up to $^1/_4$ and cooling with a freezing mixture, 1.25 g of yellow crystals, m. p. 50—57° (III), were isolated. After the evaporation and cooling of the third filtrate 0.33 g were isolated which had a m. p. 43—50° (IV).

After two subsequent crystallizations of (I) from alcohol, 1.86 g of pure *p*-dichloroazoxybenzene were obtained. After the fractional crystallization of (II), (III) and (IV) from alcohol, 1.75 g of a substance melting at 59—61° were obtained. A crystallization from ligroin raised the melting point to 61—62°. For identification this substance was converted into the already known 4-chloroazobenzene, the oxydation of which according to Angeli gave back the 4-chloroazoxybenzene. From alcohol it crystallizes in rhombic plates.

Similar results were obtained when nitrosobenzene was added gradually to *p*-chlorophenylhydroxylamine at 0—5°, as well as by the interaction of phenylhydroxylamine and *p*-chloronitrosobenzene.

4-Bromoazoxybenzenes were obtained similarly with 4-chloroazoxybenzene by the action of nitrosobenzene on *p*-bromophenylhydroxylamine. 2.65 g of pure *p*-dibromoazoxybenzene and 2.1 g of a substance melting at 60—64° were obtained. A small amount of the latter substance was converted quantitatively by usual methods into an absolutely pure 4-bromoazobenzene. The mixture of the mixed azoxycompounds was recrystallized from ligroin. 0.2 g of an isomer having a m. p. 92—93°, and 0.12 g having a m. p. 71—72° were isolated.

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Received
11. X. 1938.

REFERENCES

[1] V. O. Lukashevich, C. R. Acad. Sci. URSS, XX, № 2—3 (1938). [2] E. Bamberger u. E. Renauld, Ber., **30**, 2278 (1897). [3] E. Bamberger, Ber., **33**, 1939 (1900); E. Bamberger u. W. Bernays, Ber., **35**, 1624 (1902). [4] P. Freundler, C. R., **149**, 1135 (1909); Bull. Soc. Chim., **4**, **9**, 739 (1911). [5] E. Müller u. W. Kreutzmann, Lieb. Ann., **495**, 133 (1932). [6] W. Löb, Ber., **31**, 2201 (1898); ZS. f. Elektrochem., **5**, 456 (1899). [7] A. Angeli, Über die Konstitution der Azoxyverbindungen (1913). [8] F. J. Alway, Amer. Chem. Journ., **32**, 385 (1904). [9] P. Freundler, C. R., **143**, 910 (1906). [10] F. J. Alway, l. c. [11] W. Löb, Ber., **31**, 2201 (1898). [12] P. Freundler, C. R., **149**, 1135 (1909). [13] P. Freundler, Bull. Soc. Chim., **4**, **9**, 739—741 (1911). [14] A. Reissert u. F. Lemmer, Ber., **59**, 351—356 (1926).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

CHEMISTRY

ON SOME GENERAL PRINCIPLES WHICH CHARACTERIZE MULTICOMPONENT MUTUAL SYSTEMS

By V. P. RADISČEV

(Communicated by N. S. Kurnakov, Member of the Academy, 23. X. 1938)

Diagrams of n-dimensional compounds of $(n+1)$-component mutual systems («mutual exchange systems») may be regarded as the sections of $(n+1)$-dimensional simplexes, which represent simple systems of $n+2$ components. These sektions divide the vertices of the simplex into two groups. The n-dimensional diagram of a «displacement system» is a part of the n-dimensional simple system simplex through which a section of the above type is made. In both cases, however, the figures are of the same type, called simplex-polycoryphae. A general description of them may be found in the works of geometricians dealing with polytopes ([1],[2]). In virtue of the law of isomorphism of sections and frustums of the simplex, the only types of diagrams possible for compounds of mutual systems are those of a consecutive series of section figures. These geometric correlations are applied to physico-chemical systems in the papers of Jänecke ([3],[4]), Kurnakov ([5]), Radisčev ([6],[7],[8],[9]) and Bergman ([10], [11]); the latter compiled a table of mutual systems of up to 10 independent components inclusively.

In comparing the diagrams of compounds from various mutual systems with reference to their geometric structure and general physico-chemical properties, we feel that it is necessary to establish a rational principle for such comparison, in order to elucidate correlations which appear intricate at first sight. The distinguishing feature of mutual system diagrams is that they are formed from two groups of simplex components, which are opposite to one another, as regards chemical nature, and are situated on both sides of the section. Accordingly all the components of the mutual system (salts) consist of two kinds of ions (A and K). Each combination of the whole positive numbers A and K finds its corresponding single-valued system between possible mutual ones; the compounds of that system have a diagram of $A+K-2$ dimensions. On that account we may take a net of points with integral co-ordinates $x=K$, $y=A$, as the graphic representation of all possible mutual systems. Therefore, in order to examine any property of the mutual systems which may interest us, we can draw up a rectangular table, each square of which has one corresponding point in the net mentioned. In other cases it is expedient to construct the spatial diagram of the property as well, marking off its value along the vertical axis (z). This method of examining mutual systems, as we found, permits us to build an intuitive conception of the changes which take place in a number of their properties, and often makes it possible to forecast the values of some of the characteristic magnitudes.

In this paper we shall give the tables of some geometric properties of physico-chemical importance. These tables are based on the table of mutual system diagrams, where they are represented as simplex sections (Table 1). Each square of this table contains the symbol A/K* which shows the number of cations (K) and anions (A) the system is formed of. The sum of the two numbers of the symbol ($A+K$) gives the number of vertices in the simple system simplex, whose section is the diagram of the mutual system in question (this simplex has $A+K-1$ dimensions). A number of characteristic rectilinear directions should be distinguished in the table, viz: 1) $A=\text{const}$; 2) $K=\text{const}$; 3) $A+K=\text{const}$; 4) $A-K=\text{const}$; 5) $A/K=\text{const}$. If the const=1 for the first two directions, the line or column contains very simple sections, which are simplexes, and only beginning with const=2, the lines and columns contain mutual systems **.

Table 1

Sections through Simplexes of Multicomponent Systems which Divide the Vertices of the Simplex into Two Groups A and K

7	7/0	7/1	7/2	7/3	7/4	7/5	7/6	**7/7**
6	6/0	6/1	6/2	6/3	6/4	6/5	**6/6**	6/7
5	5/0	5/1	5/2	5/3	5/4	**5/5**	5/6	5/7
4	4/0	4/1	4/2	4/3	**4/4**	4/5	4/6	4/7
3	3/0	3/1	3/2	**3/3**	3/4	3/5	3/6	3/7
2	2/0	2/1	**2/2**	2/3	2/4	2/5	2/6	2/7
1	1/0	**1/1**	1/2	1/3	1/4	1/5	1/6	1/7
0	**0/0**	0/1	0/2	0/3	0/4	0/5	0/6	0/7
A / K	0	1	2	3	4	5	6	7

The diagonal directions intersecting both co-ordinate axes ($A+K=\text{const}$) are the lines with equal numbers of dimensions in the diagrams ($\text{const}=n+2$). Among the opposite diagonals ($A-K=\text{const}$) the main diagonal ($A=K$) is in a special position. It divides the table into two halves which are identical with regard to the structure of the diagrams in them: one half may be called «basic» (where the cations predominate) and the other—«acid» (where the anions predominate); each square of the «basic» half with the symbol p/q has

* In chemical literature this symbol is used to designate mutual systems while it has a different meaning in geometry [2].

** The «zero» line and «zero» column which contain imaginary sections of simplexes occupy a special position in the table; in this «secant» hyperplane passes outside of the simplex.

one corresponding square in the «acid» half with the symbol q/p. The diagrams of both systems p/q and q/p are identical. Table 1 is not only a table of mutual system diagrams, but also a table of their $(n-1)$-dimensional faces. It can be easily proved that the diagram of any system has only two kinds of $(n-1)$-dimensional faces, whose numbers turn out to be equal to the two numbers of the symbol p/q, which characterize the system. We have here a clear picture of the correlative correspondence between the numbers of simplex vertices on different sides of the section and the numbers of both kinds of faces of this section. It should be noted that for the main diagonal in the table ($A=K$) both kinds of section faces become identical. Special interest is due to the squares situated next to some given one and containing figures of $n-1$ and $n+1$ dimensions, since the first two give $(n-1)$-dimensional faces of the section of the square given, and the second two give the figures into which the section divides the $(n+1)$-dimensional simplex*.

Of the property tables let us first of all examine the table of stable cells (of secondary simplexes), into which the secant complex, which consists of stable $(n-1)$-dimensional simplexes, divides the mutual system diagrams (the stable diagonals of the squares of mutual couples form the base of the secant complex)**.

The author of this paper studied the stable complexes of mutual systems with 4, 5 and 6-dimensional diagrams (5, 6 and 7 independent components) from the geometry and the physico-chemical viewpoint. The data for quinary systems have already been published ([8],[9]), and those for more complex systems are being prepared for publication. If we take from those data the numbers of stable cells for the diagrams of various systems, and compile a table after the method given above, we shall observe that the numbers of cells form Pascal's triangle (Table 2). The geometry sense of this fact needs special investigation; for the time being we shall only point out a purely empiric law***. However, this law stands out quite clearly, which apparently gives us the right to continue compiling tables after Pascal's triangle law up to any number of components, and to foretell number of cells for any system. From this principle it follows that the number of cells for any diagram is equal to the total number of all the cells for each kind of $(n-1)$-dimensional face in it. On the other hand, Table 2 also gives us the number of cells in both halves of the simplex, if the section of the given mutual system has been drawn through it (we get all these data from the «surroundings» of square in question).

Further, let us turn our attention to the problem of the number of $(n-1)$-dimensional secant stable simplexes (the «stable diagram screens»). This number (P) can be found for any diagram from the equation: $S=\frac{\alpha_{n-1}+2P}{n+1}$, where α_{n-1} is the total number of cells on the $(n-1)$-dimensional faces of the diagram, S — the number of n-dimensional cells in the diagram, and $n+1$ — the number of $(n-1)$-dimensional faces of the n-dimensional cell.

Without giving the table of the numbers of secant simplexes, we shall point out that the ratios of these numbers to the numbers of cells obey an empiric law in each diagram. If we compile a table of such ratios (z) for a number

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* In the symbols of the first line ($A=1$) and the first column ($K=1$) which characterize the section simplexes, imaginary faces which belong to the zero line or the zero column are formally also taken into account.

** All these stable elements determine the general structure of the state diagram of the system, their practical importance is therefore beyond doubt.

*** We here remind the reader that Pascal's triangle expresses a number of numerical regularities pertaining to simple multicomponent systems; these facts were noted by N. S. Kurnakov ([5]).

Table 2

Number of Stable Cells in the Simplex Sections of Multicomponent Systems

7	1	7	28	84	210	462	**924**
6	1	6	21	56	126	**252**	462
5	1	5	15	35	**70**	126	210
4	1	4	10	**20**	35	56	84
3	1	3	**6**	10	15	21	28
2	1	**2**	3	4	5	6	7
1	**1**	1	1	1	1	1	1
A / *K*	1	2	3	4	5	6	7

of systems (Table 3)*, we find that their dependence upon A and K may be expressed by the following quadratic equation:

$$z = \frac{AK - K - A + 1}{A + K - 2} \quad **.$$

Ratios of the Secant Simplex Numbers to the Numbers of Cells

Table 3

7	0	6/7	12/8	18/9	24/10	30/11	**36/12**
6	0	5/6	10/7	15/8	20/9	**25/10**	30/11
5	0	4/5	8/6	12/7	**16/8**	20/9	24/10
4	0	3/4	6/5	**9/6**	12/7	15/8	18/9
3	0	2/3	**4/4**	6/5	8/6	10/7	12/8
2	0	**1/2**	2/3	3/4	4/5	5/6	6/7
1	**0**	0	0	0	0	0	0
A / *K*	1	2	3	4	5	6	7

* In Table 3 these ratios are shown in the form of fractions which are reduced to a common denominator in each diagonal ($A+K$=const) line.

** By using this equation it is easy to calculate the number of secant simplexes P for any diagram, since $R=zS$, where S is the number of stable cells.

A study of this equation will show that it represents a circular cone whose vertex corresponds to the co-ordinate numbers $A=1, K=1, z=0$*. It is clear that the only real points on this surface are those which correspond to whole and positive value of A and K.

The rectilinear elements of the cone (in its «realized» part) are situated above the rays of plane $[AK]$, which issue from the cone's vertex and for which the ratios $\frac{A-1}{K-1}$ are constant. We get an especially simple series of values for z in the main diagonal of the table ($A=K$), viz. 0; 0.5; 1; 1.5; 2 etc. Sections of the cone ($\parallel$ axis z), in the direction of like dimensions ($A+K=$const) are parabolas with their vertices situated above the main diagonal, and show that here the ratio z is at its maximum value at the figure of the main diagonal. It should be noted that the ratio z is unity for only one figure, namely, for the one with 4 dimensions and 9 vertices ($A=3$, $K=3$).

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Received
29. X. 1938.

REFERENCES

[1] P. H. Schoute, Mehrdimensionale Geometrie, II, Leipzig (1905). [2] D. M. Y. Sommerville, An introduction to the geometry of N dimensions, London (1929). [3] E. Jänecke, Heidelberg. Akad. Sitz., Jahrg. 1930. 15 Abh. (1931). [4] E. Jänecke, Z. anorg. u. allg. Chem., **196**, 337 (1931). [5] Н. С. Курнаков, Изв. Сект. физ.-хим. Акад. наук, VIII (1936). [6] В. П. Радищев, ЖОХ, **5**, 455 (1935). [7] В. П. Радищев, Изв. Сект. физ.-хим. Акад. Наук, IX, 219 (1936). [8] В. П. Радищев, там же, IX, 203 (1936). [9] В. П. Радищев, Изв. Акад. Наук СССР, сер. хим., № 1, 153 (1936). [10] А. Г. Бергман, ЖОХ, **5**, вып. 3 (1935). [11] А. Г. Бергман и Н. С. Домбровская, Изв. Акад. Наук СССР, сер. хим., № 1, 133 (1936).

* The canonic equation of the cone referred to another co-ordinate system is $\frac{x^2}{2}+\frac{y^2}{2}-z^2=0$; the cone has an obtuse angle at its vertex, equal to 109°28′2″7.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

CHEMISTRY

ON SOME PHYSICO-CHEMICAL PROPERTIES OF MULTICOMPONENT MUTUAL SYSTEMS

By V. P. RADISČEV

(Communicated by N. S. Kurnakov, Member of the Academy, 23. X. 1938)

In our last paper (1) we gave tables for some of the geometric properties of the diagrams of compositions of multicomponent mutual systems. Here we shall briefly touch upon some principles of a physico-chemical nature which are observed in the diagrams mentioned and are closely connected with their geometric structure.

In comparing the diagrams of the compounds of various systems we cannot but notice that the components differ in their capability of entering into exchange reactions with one another. Thus, the components of systems from the 1st line (or 1st column) of the basic table of the system, which was given in the last report (1), do not enter into interchange reactions with one another at all. The interacting components of systems from the 2nd line (2nd column) divide up into two groups (simplexes), and the members of each group cannot enter into exchange reactions among themselves; this is in close connexion with the prismatic structure of such diagrams. Systems from the 3rd line (3rd column) have more possibilities for exchange reactions than systems from the 2nd line (2nd column), etc.

In order, thefefore, to characterize the interaction of components of the system quantitatively, it is expedient to introduce a special magnitude—«the completeness of interaction» (R), which may be defined as the ratio of the number of mutual couples (B) to the number of salts (N)*. The number of mutual couples in different mutual systems can easily be calculated by the formula: $B=\binom{A}{2}\cdot\binom{K}{2}$, where A is the number of anions, and K the number of cations. The number of salts can be calculated by the formula $N=AK$. The values of «completeness of interaction» (R), obtained in this manner, are given in Table 1. A study of the table shows that R can be expressed as a function of A and K in a quadratic equation $(A-1)(K-1)=4R$. This equation represents the surface of a hyperbolic paraboloid, constructed above plane $[AK]$. It is clear that the only points of this surface, which become «realized», are those which correspond to whole and positive values of A and K. Sections of the surface ($\|$ axis R) in the direction of the lines $A=$const and $K=$const are straight lines; hence it follows that R increases within the limits of every line or column of the table, as a linear function

* Thus, in system 2/2 there is one mutual couple to 4 salts; in system 2/3—three mutual couples to 6 salts; in system 3/3—nine mutual couples to nine salts, etc.

of the number of dimensions of the figure (since the number of dimensions $n=A+K-2$). Sections in the direction of the line $A+K=$const are parabolas with their vertices situated above the main diagonal of the table ($A=K$); they show that among systems with the same number of dimensions R is the greatest for the system of the main diagonal. The sections for $R=$const, which are equilateral hyperbolas, also show that the systems of the main diagonal have extremal properties. In general it may be stated that the increase of R is influenced by two factors, viz: 1) the increase in the number of dimensions of the diagram and 2) passing upwards from the lower lines (the columns) in the table to the higher*.

Table 1

The „Completeness of Interaction" for Multicomponent Mutual Systems

7	0	1.50	3.0	4.5	6.0	7.5	**9.0**
6	0	1.25	2.5	3.75	5.0	**6.25**	7.5
5	0	1.0	2.0	3.0	**4.0**	5.0	6.0
4	0	0.75	1.5	**2.25**	3.0	3.75	4.5
3	0	0.5	**1.0**	1.5	2.0	2.5	3.0
2	0	**0.25**	0.5	0.75	**1.0**	1.25	1.5
1	0	0	0	0	0	0	0
A / K	1	2	3	4	5	6	7

The second principle which we shall examine in this report is one of a thermodynamic nature. In previous papers ([2], [3]) the author pointed out that it is necessary to distinguish between independent stable diagonals of the mutual couples of any complex mutual system (diagonals of the first power) and dependent ones. The maximum reaction works for the latter are in value the sums of the works for some of the former, i. e. the works of the independent diagonals are **components**, which make up the works of all the rest of the diagonals (analogous relations are observed for the thermal effects of exchange reactions). Thus, in system 2/3 two of the three diagonals are independent; in system 2/4 three of the six diagonals are independent; in system 3/3 four of the nine diagonals are independent, etc. The independent diagonals can be detected by purely geometrical signs. If we construct schematic diagrams for different mutual systems after the same principle and represent in their stable complexes of the same simplest type, it will be easy

* It should be noted that the number of salts (N) in mutual systems can also be expressed as a function of A and K in the form of the surface of a **hyperbolic paraboloid** with the equation $N=AK$; the number of mutual couples (B) is represented by a **surface of the 4th order**: $B=\frac{1}{4}AK(A-1)(K-1)$.

to deduct from the diagrams the number of independent diagonals for each system (we cannot go into these constructions and deductions here, we shall do so in a separate article)*. If we compile a rectangular table of the numbers obtained in this manner (Table 2), we shall observe a simple principle in their formation. Here we again get the surface of a hyperbolic paraboloid with the equation $(A-1)(K-1)=L$, where L is the number of independent diagonals, A—the number of anions and K—the number of cations. In examining the table, we see that L increases linearly within every line or column; among systems with diagrams of the like dimensions L reaches its maximum in the system of the main diagonal of the table ($A=K$) and decreases according to a parabolic curve as the difference $A-K$ increases. For the main diagonal of the table the values of L are the squares of the numbers of the natural series. The ratios (Q) of the numbers for all the diagonals to the numbers of the independent ones may also be expressed by the equation of a hyperbolic paraboloid: $Q=\frac{1}{4}AK$. From the corresponding table, which we are not giving in this paper, it is obvious that Q increases as the number of dimensions and as we go upwards from the lower lines (the columns) towards the upper ones. Thus, in system 2/2 $Q=1$, and in system 8/8 $Q=16$; we see that as the diagram becomes more complex in the two respects mentioned, the number of independent diagonals, which increases comparatively moderately, gives birth to an ever increasing variety of exchange reactions.

Table 2

Number of Independent Diagonals in the Diagrams of Multicomponent Mutual Systems

7	0	6	12	18	24	30	**36**
6	0	5	10	15	20	**25**	30
5	0	4	8	12	**16**	20	24
4	0	3	6	**9**	12	15	18
3	0	2	**4**	6	8	10	12
2	0	**1**	2	3	4	5	6
1	**0**	0	0	0	0	0	0
A / *K*	1	2	3	4	5	6	7

There is a close relation between the «completeness of interaction» (R) described above and its number of independent diagonals (L). As may easily

* These deductions are certainly correct for the type constructed. However, as a study of stable complexes for simpler systems (with 5 and 6 independent components) showed, the number of independent diagonals remains invariant for different types of the same systems. Hence it may evidently be taken that this invariance will remain in more complex systems.

be deduced from the equations given above, this relation can be expressed very simply:

$$L = 4\frac{B}{N} = 4R.$$

Institute of General and Inorganic Chemistry.
Academy of Sciences of the USSR.

Received
29. X. 1938.

REFERENCES

[1] V. P. Radiščev, C. R. Acad. Sci. URSS, XXI, № 8 (1938). [2] В. П. Радищев, Изв. Сект. физ-хим. Акад. Наук, 9, 203 (1936). [3] В. П. Радищев, Изв. Акад. Наук СССР, сер. хим., № 1, 133 (1936).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

CHEMISTRY

ON THE TOPOLOGICAL STRUCTURE OF THE STABLE COMPLEXES OF MULTICOMPONENT MUTUAL SYSTEMS AND THE CLASSIFICATION OF THEIR DIAGRAMS

By V. P. RADISČEV

(Communicated by N. S. Kurnakov, Member of the Academy, 23. X. 1938)

In paper (1) we pointed out that the basic diagram table of components of mutual systems is divided into two identical halves along the main diagonal ($A=K$). Consequently, all the possible general types of diagrams are represented in one of the halves (for instance, the lower right-hand one). This half is divided up into horizontal rows which begin with the system of the main diagonal; the numeration of the rows is determined by the number of ions of the same sign, which remains constant within the row. The first row contains simplexes, which are not mutual systems; the latter begin with the second row. Dividing the systems into such rows is justified by many common signs shown by the systems of each row*. Thus, those values which are peculiar to the systems and are represented above plane $[AK]$ as the surface of hyperbolic paraboloids (2), change linearly within each row (the number of salts, the number of independent diagonals, the ratio of the total number of diagonals to the number of the independent ones, completeness of interaction). The structure of the diagrams of compounds and of stable complexes for systems of the same row prove to be quite similar to each other. Thus, for instance all the diagrams of systems belonging to the 2nd row are simple prisms (of the first type) with two simplexes as the bases and prisms as side faces. The complexes of secant $(n-1)$-dimensional simplexes have the simplest construction in these figures and have no «extra» simplexes of lower orders (i. e. such as could not be present in the side faces of the diagram)**. Here the number of secant simplexes is always one less than the number of stable cells (1).

The diagrams of the next rows are more complex polytopes (not prisms). The number of secant simplexes in them is greater than the number of cells (with one exception, in which these numbers are equal). Here there appear in the stable complexes «extra» simplexes of lower orders, which are mainly made up of stable diagonals (and partly of the edges of the polytope).

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* On the other hand, if we examine the diagrams of equidimensional systems, we notice that a number of figures differ considerably.

** The structure of the diagrams of systems belonging to various rows will be described in a special article; see also (3) and (4).

These simplexes contain all the kinds of ions of the system, and are therefore internal figures which do not belong to the outher faces of the polytope; they form at the same time as the $(n-1)$-dimensional secant simplexes and are closely connected with the latter. This connexion is manifest in the

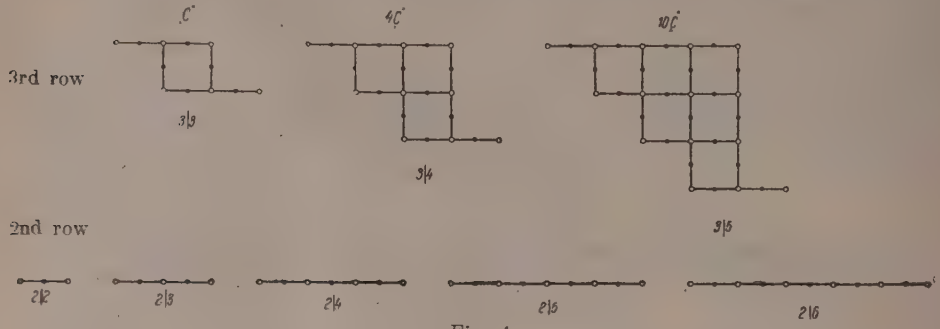

Fig. 1

fact that they are the carriers («axes») of pencils and sheaves of secant simplexes*.

In the systems of the third row only $(n-2)$-dimensional «extra» simplexes appear as the axes of pencils of spaces of $(n-1)$-dimensional secant simplexes. Thus, in system 3/3 one «extra» triangle appears**; in system 3/4 three «extra» tetrahedrons appear; in system 3/5 six «extra» pentatopes, etc.

In systems of the 4th row, there are also $(n-3)$-dimensional «extra» simplexes formed alongside of the $(n-2)$-dimensional ones, as it may be inferred from the diagram of system 4/4. Thus, in system 4/4 (16 «C»—see below) there are 12 «extra» pentatopes and one «extra» tetrahedron. The first are the «axes» of pencils of $(n-1)$-dimensional secant simplexes; the second accounts for the appearance of space sheaves of various stable simplexes (with $n-2$, $n-1$ and n dimensions), of which it is a component.

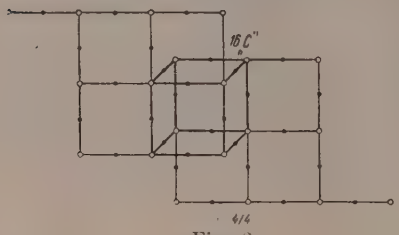

Fig. 2.

We may assume that «extra» simplexes of $(n-4)$, $(n-5)$, etc. dimensions will appear in the systems of the next rows, along with the higher ones.

These correlations can be represented schematically by constructing such diagrams as will show how the n-dimensional cells are held together by the $(n-1)$-dimensional secant simplexes. The starting point to build up these diagrams lies in an analysis of the diagrams of the respective systems. Such complexes of stable cells for the 2nd and 3rd row are shown in Fig. 1 and for the system 4/4 (4th row)—in Fig. 2***. These figures show the simp-

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* Besides the secant simplexes which are bound in pencils, polytopes may have secant simplexes which are not thus bound; the latter are always separated by «free vertices», i. e. such as have no diagonals.

** For instance, in the system Na_2, Tl_2, Ca/Cl_2, SO_4, $(NO_3)_2$ the triangle $CaCl_2$—Na_2SO_4—$Tl_2(NO_3)_2$ should be taken as such (on the basis of thermochemical data).

*** The complexes of stable cells are the basis of the crystallization «tree» in the fusibility diagrams of the respective systems, since (if there are no continuous solid solutions) each n-dimensional cell has a corresponding $(n+1)$ times repeated invariant point (p=const). Crystallization trees were first constructed for some multicomponent mutual systems (after the combination method) by Bergman (partly in collaboration with Dombrovsky) [5,6].

lest (the most regular) stable complexes for the 3rd and 4th rows, which are obtained when all the 4-dimensional 9-coryphae, entering into the diagram of the system, belong to the same structural type «C» ([4]). On all the figures the white circles represent n-dimensional stable cells, and the black ones—$(n-1)$-dimensional secant simplexes. We see that in systems of the 2nd row the cell complexes are simple trees, which may be considered monodimensional figures (belonging to one straight line). The appearance of plane cycles is peculiar to systems of the 3rd row, and the whole complex in this case is represented by a plane figure. Each cycle in this case encircles a separate pencil of $(n-1)$-dimensional secant simplexes. The number of cycles corresponds to the number of «extra» $(n-2)$-dimensional simplexes. The side offshoots are formed by the extreme cells in the diagram; the secant simplexes which separate them are not bound in pencils (the number of offshoots corresponds to the number of «free» vertices in the diagram).

In system 4/4 (4th row) the complex is represented by a figure of three dimensions, since a space cell makes its appearance in this case (Fig. 2). There are 12 plane cycles in this figure with 12 pencils of $(n-1)$-dimensional secant simplexes at their bases (in this case, hexatopes of 5 dimensions).

Six of the cycles mentioned compose a space cell. The cells form under the agency of an «extra» simplex of $n-3$ dimensions (a tetrahedron), since the latter is the carrier of space sheaves of the elements which form it. We may assume that the number of space cells in the other systems of the 4th row will increase with the number of $(n-3)$-dimensional «extra» simplexes.

We obviously have reason to expect that 4-dimensional cells should appear in the next row (the fifth), 5-dimensional cells in the sixth etc. (since «extra» simplexes of $n-4$, $n-5$, etc. dimensions appear).

We shall discuss the problem of the isomery of cell complexes in a separate paper.

Institute of General and Inorganic Chemistry.
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Received
29. X. 1938.

REFERENCES

[1] V. P. Radiščev, C. R. Acad. Sci. URSS, XXI, № 8 (1938). [2] V. P. Radiščev, ibid., XXI, № 8 (1938). [3] В. П. Радищев, Изв. Сект. физ.-хим. Акад. Наук, **9**, 203 (1936). [4] В. П. Радищев, Изв. Акад. Наук СССР, сер. хим., № 1, 153 (1936). [5] А. Г. Бергман, ЖОХ, **5**, вып. (1935). [6] А. Г. Бергман и Н. С. Домбровская, Изв. Акад. Наук СССР, сер. хим., № 1, 133 (1936).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

PHYSICAL CHEMISTRY

INFLUENCE OF SURFACE-ACTIVE SUBSTANCES ON STRUCTURE FORMATION IN GELATIN SOLS

By K. F. ZHIGATCH, P. A. REHBINDER, Corresponding Member of the Academy, and G. G. EDELMAN

Investigation made in our laboratory ([1],[2],[3]) has shown that surface-active substances markedly affect the structure formation (and setting) in solutions of lyophile colloids when added to the latter. This was demonstrated with especial clearness for hydrocarbon systems ([3]). The present work is concerned with the influence of surface-active substances in aqueous solutions, this question being linked with the general problems of the rôle of surface activity in lyophile colloids. In studying the formation kinetics of the adsorption layer at the surface in solutions (in water for a number of hydrophile colloids), we established that their surface activity ([4]), i. e. the decrease in static (equilibrous) surface tension caused by them, is an important feature of the colloidal (volume) properties of these sols, as it is of their surface properties (i. e. foam forming, wetting, stabilizing and dispersive influence, etc., aside from the mechanical properties of adsorption layers) ([5]). Table 1 gives the equilibrium values of surface tension for some aqueous solutions of hydrophile colloids, which we estimated after the method of the bubble pressure ([4]) at 20° C (for pure water $\sigma = 72.75$ erg/cm²).

Table 1

Colloid	C, %	Static. σ erg/cm²	$\Delta\sigma = \sigma_0 - \sigma_c$	τ (in min.)	Capability of jellifying
Agar-agar	—	72.75	0.0	Does not depend on time	Jellifies
Starch	0.1	71.0	1.8	Fractions of a second	»
Gelatin	1.0	62.0	10.8	20	»
Albumin	0.1	52.2	20.6	30	Does not jellify
Tragacanth soluble	0.5	51.4	21.4	20	» » »
Saponine	1.5	41.8	31.0	10	» » »

τ is the time (of the bubble formation) which is necessary for the static surface tension to form, C—the percentage sol concentration taken

at the point where the surface tension reaches its minimum which value does not change as the sol concentration is further increased.

From Table 1 it follows that the surface-active colloids (albumin, the soluble part of tragacanth, saponine) do not set in aqueous solutions, while the surface-inactive (starch, agar-agar) or comparatively little active ones (gelatin) act contrariwise *.

Further studies were concerned with the surface activity of albumin fractions. They have shown the surface-active part of albumin to be made up of those fractions which do not coagulate when albumin solutions are heated to 60°, i. e. of more highly dispersed ones.

In the surface-inactive colloids (starch, agar-agar) the polar and non-polar groups are apparently arranged symmetrically, both in the elementary molecules (for instance, in polysaccharides) and in micellae, and therefore all the fractions of such colloids are surface-inactive. But the case of surface-active colloids (proteins, saponin) is much more complex: the elementary molecules (for instance, aminoacids) are surface-active, and the more asymmetrically the polar and non-polar groups are arranged, the greater the activity of the molecules.

After the micellae have reached a certain degree of aggregation, their surface activity begins decreasing with further aggregation, since the latter promotes the symmetrical distribution of polar and non-polar groups in a large micella. Greater symmetry may be attained, for instance, if the polar groups are bound together into an internal hydrophile nucleus. Thus, surface-active colloids are mixtures of fractions of different surface activity. Naturally enough, we find those surface-active hydrophile colloids to set easily which consist chiefly of symmetrically constructed micellae, capable of an intense volume hydration.

Structure formation is obviously the more difficult, the higher the concentration of the surface-active fraction in a given sol, which is connected with raising of the general surface activity of the latter. The investigation made by S. M. Liepatov and his coworkers ([6]) on the influence of soluble fractions of gelatin upon structure formation in its sols are no doubt in close contact with this phenomenon.

When the surface activity of a colloid is increased, setting is generally hampered, since the relative content of structure-forming part is reduced. But besides this surface-active substances may directly hamper setting in an aqueous medium. To throw light upon this phenomenon, we studied the change of structural viscosity with time in 0.75 and 0.5% gelatin (Gold Brand) sols in the presence of admixtures of saturated alcohols (of the normal series). 0.5 and 0.75% gelatin sols were prepared in aqueous solutions by heating weighed portions of gelatin to 40° C over a water-bath. The relative viscosity (related to water) of these solutions was measured in Ubbehllode's viscosimeter 1, 24, 48, 72 and 96 hours after the solutions had been prepared (the solutions were kept and measured at 20° C). The pH of the solutions was fairly constant in all cases (6.7—6.8).

Poiseuille's law was verified for the flow of each sol through capillary tubes. The relative viscosity was measured at various pressures (100, 200, 300, 400 mm of water). The capillary tubes of the viscosimeter satisfied the condition of laminar flow (or Reynolds' condition, if there was no structural viscosity). In each series of experiments the sol was first forced through a capillary tube the number of times necessary to get a constant outflow time for the sol at the respective pressure. The results of measuring are given in Tab-

* Surface-active admixturesin starch seem to account for its very little surface activity.

le 2. They show that the action of surface-active, molecularly soluble admixtures in gelatin is analogous to that of surface-active micellar fractions, which hamper structure formation. In a number of alcohols this action of admixtures increases with the surface activity. For the mechanism of the structural formation, necessary for the sol to change into a lyogel at setting, the following two schemes may be examined.

Table 2

Solution	Relative viscosity and its changes in the course of ageing (P=200 mm H_2O at 20°C) time in hours					Change in relative viscosity as pressure P rises
	1	24	48	72	96	
Gelatin sol without admixture { 0.50%	1.43	2.98	4.88	6.92	8.66	The structural viscosity falls as P rises
Gelatin sol without admixture { 0.75%	1.47	5.55	—	159.4	168.0	
0.5% sol in a 0.5 molar solution of ethyl alcohol	1.48	1.62	—	1.79	1.70	No changes; absence of structural viscosity
0.75% sol in a 1.0 molar solution of ethyl alcohol	1.62	4.95	—	55.2	91.4	Structural viscosity falls as P rises
0.5% sol in a 0.5 molar solution of propyl alcohol	1.53	—	—	2.22	2.08	No changes; absence of structural viscosity
0.75% sol in a 1.0 molar solution of propyl alcohol	1.75	2.56	2.66	2.73	3.51	Do
0.5% sol in a 0.5 molar solution of buthyl alcohol .	1.60	—	1.53	—	1.61	»
0.75% sol in a 1.0 molar solution of buthyl alcohol	1.82	2.05	—	2.26	2.30	»
0.5% sol in a 0.5 molar solution of urea	1.43	—	1.42	—	1.50	»
0.75% sol in a 1.0 molar solution of urea	1.47	1.59	1.70	1.79	1.79	»

1. Setting may occur as a result of strong volume solvation-swelling and surface-solvation in the sol particles—development of the solvate films which possess high mechanical properties. As a result of this the particles are brought closer together until they are separated by nothing but solvate coats, and the system turns into a quasi-solid jelly. This kind of setting takes place, for instance, in stable emulsions: if the volume of the dispersed phase in them increases (in the lyophile colloid this occurs as a result of volume solvation), displacement elasticity, which characterizes the structure, appears during the transition into the foam-like state, i. e. when the droplets, which are separated only by thin films, come into contact.

2. Setting may occur as a result of there being non-solvated portions on the surface of the micellae along which the particles do aggregate, and which are greatly solvated (by volume) by the dispersion medium (6).

Thus, the basis of jellying in both schemes is strong volume solvation.

When surface-active substances are introduced into an aqueous solution of a hydrophile colloid, their polar groups unite with the polar groups of the micellae, thus acting dehydratively (7), i. e. decreasing solvation both with

regard to surface and volume. The hydrophile micellae grow hydrophobe, and therefore it becomes difficult for gels to form.

In measuring the adsorption of alcohol by gelatin, we found that 1 g of gelatin holds at maximum 0.018 moles (about 1.6 g of *n*-buthyl alcohol) in a 0.1 sol. These results are of interest in connexion with the well-known dehydrating and coagulating action of alcohols in high concentrations on protein sols.

It is of interest to note the strong influence displayed by urea over structure formation in gelatin sols, which is apparently connected with the chemical action of amine groups.

The investigation is still in progress.

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Received
16. X. 1938.

REFERENCES

[1] П. А. Ребиндер, Изв. Акад. Наук, сер. хим., No 5, 639 (1936); сб. Совр. проблемы колл. химии в кожев. промышленности, 75 (1937). [2] P. Chomikowski u. P. Rehbinder, Acta Phys. Chim., VIII, № 3 (1938). [3] П. А. Ребиндер и В. В. Маргаритов, Ж. резин. пром., No 11 (1935); V. Margaritov, Acta phys.-chim., VIII, № 3 (1938). [4] К. Ф. Жигач и П. А. Ребиндер, Ж. Физ. хим., No 12 (1938); К. Ф. Жигач, Зав. лаборат. No 6, 700 (1937). [5] A. A. Trapeznikov a. P. A. Rehbinder, C. R. Acad. Sci. URSS, XVIII, No 3 (1938); No 7 (1938); P. A. Rehbinder a. A. A. Trapeznikov, ibid., XVIII, No 7 (1938); Н. М. Лубман, Ж. Физ. хим., I, No 6, 721 (1930); III, No 2—3, 204 (1932). [6] С. М. Липатов, Усп. химии, **4**, 933 (1935); сб. Совр. проблемы колл. химии, **5** (1937); Колл. журн., III, вып. 8, 704, 712 (1937). [7] D. A. Sawnders, Biochem. J., I, 31, 1093 (1937); Br. Jergensons, Kolloid-Beihefte, **44**, 8—12 (1936).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

STRATIGRAPHY

NEOCOME AND JURASSIC DEPOSITS IN THE LAGICH MOUNTAINS OF AZERBAIDJAN

By N. B. VASSOEVICH

(Communicated by A. A. Borissiak, Member of the Academy, 10. XI. 1938)

The southern slope of the Main Caucasus Range, extending over a considerable distance away from the wide Alazan river valley on the west, up to the village Vandam on the east, is not distinguished by any appreciable and isolated foothills. Within 15—20 km from the watershed area of the Main Caucasus Range, with absolute marks 2500—4500 m up to the Alazan-Agrichai and Vandam-Nuha valleys (500—600 m above the sea level), a rapid lowering of all spurs takes place. The torrential mountain streams, with waterfalls and rapids in their upper parts, emerging freely from gorges into the wide expanse of the piedmont depression, carry off innumerable pebbles and form huge cones of wash-out deposits.

East of Vandam there is a sudden change of scenery: running parallel to the Main Ridge, there evolves an orographical uplift known in literature as the Lagich mountains or the Nial-dag ridge. It exhibits its greatest prominence east of the parallel of the village Ismailla, where peaks of 2000—2290 m above sea level are manifest. The eastern extremities of the mountains lie beyond the river Akhu-su, at the village Chukhur-Yurt.

The river Gerdyman-chai, dissecting the Ridge practically in the middle, forms a narrow gorge with a path running on its steep slope up to the village Lagich, located in a depression (circular valley) north of the mountains, bearing an identical name.

The first explorers of the south-eastern part of the Main Caucasus Range, H. Abich, Shegren and K. I. Bogdanovich ([1]), paid little attention to the structure of the Nial-dag range. Bogdanovich referred all formations developed at that locality to the «Orbitoidal series» (Upper Senonian), plotting on the map separately «the andesites and their tuffs», while actually to the Maastricht refers only an insignificant portion of the deposits composing the syncline at the village Namazgia and the Nial-dag pass (these strata containing *Orbitella apiculata* Schlumb. were either completely ignored by subsequent explorers or erroneously qualified as Turonian).

During the recent years, the Lagich mountains, distinguished by their curious structure, have once more attracted the attention of a number of geologists. In 1934 the central part of the range was mapped out on the scale of 1 : 84 000 by V. E. Khain, who was the first to give an essentially correct scheme of the stratigraphy of Cretaceous deposits composing the range ([4]). In 1935 the Nial-dag range was studied by means of route intersections

by V. V. Weber ([3]) and Z. A. Mishunina ([3]). The results of their investigations corroborated the stratigraphic scheme designed by Khain.

The oldest strata among those recognized by the above-mentioned geologists in the Lagich Mountains have been assigned to the Lower Albian or Aptian. Higher up there appeared distinct series of chiefly tuffogeneous accumulations, with single covers of porphyrites (Albian-Cenomanian), overlain by siliceous-carbonate rocks of the variegated Nial-dag horizon (base of the Turonian) and of the Kemchi series.

In September 1938, while studying the Cretaceous deposits of the southern slope of the Main Caucasian Ridge (on request of the Azerbaidjan Scientific Research Institute) I was walking along the gorge of the river Gerdimanchai, from the village Sardagar to the village Lagich, i. e. following the route of all geologists who had been previously working there. Having but very little time at my disposal, I could stop only for a few hours at the village Gyandova, situated in the middle part of the gorge. I was interested in the age of the Flysch beds which had been isolated here by Khain ([1]) and referred by him to the Clanseian. As a result of survey work, new data were derived permitting to establish the existence of much older formations in the Lagich mountains than those hitherto known.

Along the river Kiash-chai (the right tributary of the river Gerdymanchai, discharging its waters into the latter at the village Gyandova), about 1 km above its mouth, near the first inaccessible waterfall, I have recorded the following section (from the bottom upwards):

1. Frequent interstratification of brownish-red and dirty greenish grey tuffogenic compact and solid alevropelites and psammites, without sharply defined limits between layers. Single interbeds show a brecciated texture. All the rocks are non-calcareous. From a distance this bed-pack shows external resemblance with the variegated Kyzyl-Kazmin (Khaltan s. str.) series ([2]). Visible thickness—7—8 m.

2. Tuff-breccia with single large fragments of tuffogeneous rocks and volcanic tuffs up to 50 cm in diameter. This tuff-breccia comes into contact with the first bed-pack along an irregular plane with traces of wash-out. Thickness about 3 m.

3. White and whitish limestones, in places rather pure, cryptocrystalline, of the «Dibrar type» (i. e. of the type of Upper Jurassic limestones of which frequently the Dibrar cliffs—«Klippen»—are composed), and sometimes marly, mottled and striated, with irregular «sticks» of subsiltstone areno-calcareous material (i. e. limestones of the «Satibine» type). In the limestones occur calcified *Radiolaria* and occasionally faintly discernible *Calpionella*(?).

From the exposure it may be clearly seen, how the limestone pack unconformably overlies the tuff-breccia along an uneven plane. Single fragments, boulders and pebbles of porphyrites and their tuffs are found both in the limestones and in the lenticular interbeds of fine conglomerates, occurring sporadically among limestones. Along fissures in calcite veins, there were faintly recognizable «sticks» of liquid earth oil with a kerosene odour. Thickness about 3 m.

4. Upwards the rocks are gradually darkening, while the series as such becomes more variegated in its composition. There appear bands of brown, slightly bituminous marls, bleached on the surface through weathering, beds of marly conglomerates composed of fragments of limestones and various, mostly greenish, tuffogeneous rocks; in the interstratified microconglomerates, which are of varying thickness depending upon the change of the strike, there were revealed aptychus and organogenic detritus. Aptychus occur also in pelitomorphous limestones. Thickness exceeding 10 m.

5. There is a gradual transition of the foregoing beds into marly Flysch, characterized by a more or less clearly pronounced rhythm in interstratification of microconglomerates, granulated (to a certain degree arenaceous) limestones, compact marly limestones (rocks prevailing at the base of the described bed-pack), marls and marly shales, subsiltstones, grading into argillites, etc. Single interbeds contain spicules of siliceous sponges and show silicification. The thickness of the series measures some tens of meters.

The described series with a typical Flysch aspect in its visible upper parts, while dipping at low angles eastward, is occasionally strongly undulated and dissected by faults.

Not far from the mouth of Kiash-chai, the layers exhibit a sharp bend, and forming an upturned, nearly recumbent syncline, appear farther in reversed position. Thus, near the last hut of the village Gyandova (at the lower course of Gerdyman-chai) lies an overturned series, typical for the Nardaran Flysch, interbedded with limestones, marls and shales, with single bands of argillites, dipping SE 140°∠40—45°. The same attitude is exhibited also on the left bank of Gerdyman-chai, opposite the village Gyandova, as well as above the same, where the beds are sometimes more gently sloping, dipping to NE.

The stratigraphic position of the lower horizons of the limestone series, transgressively overlying the tuffogenic beds, may be easily determined by correlation with sections through the adjoining regions: they represent the basal parts of the Nardaran series (²), referring in age to the Upper Tithonian and Lower Valanginian. This is exactly the series, characterized by identical forms of aptychs, which have been observable at the river Kiash-chai as well. The limestones as such are very remarkable too: now of the «Dibrar», now of the «Satibine» type, containing calcified *Radiolaria*, whereas the overlying thick beds of Flysch correspond to the middle and upper horizons of the Nardaran series. Thus, in the section across Gerdyman-chai, those layers which had been previously assigned to the Albian or Aptian, actually belong to the Lower Neocome and form a syncline overturned eastward. On the other hand, the tuffogeneous rocks, cropping out near the waterfall on the river Kiash-chai, being formations older than the Nardaran series, may be referred only to the Jurassic. It seems most natural to regard these rocks as analogous to the so-called «porphyrite Jurassic», widely developed both in the Little Caucasus and in Western Georgia, and referring in age to the lower part of the Dogger (the latter understood in a broad sense, as used by Alb. Heim and M. Gignoux). Single outcrops of the same «porphyrite Jurassic» are traceable also westward of the described region both at the foot of the Main Caucasus Range (for instance, at the village Kakh) and farther away, throughout the continuation of the buried Kakhetia range. In 1936 outcrops of the «porphyrite Jurassic» were identified by me in the region of the village Ziteli-Zkharo (at the mountain «Dva Brata» and in other places). Individual outcroppings of the effusive tuffs of Dogger and limestones of the Upper Jurassic (and of the Lower Neocome?), in the strip extending from the Kakhetia range to Gerdyman-chai, bear evidence that there had existed (at least, up to the end of the Eocene) an uplift—the Kakhetia-Lagich cordilleras, formed during the Upper Jurassic period of diastrophism. It is rather curious, that according to their facies and correlations between single horizons of the Cretaceous and the Paleogene, the Lagich mountains bear close similarity to the Kakhetian zone of Eastern Georgia. The former, as well as the latter, display considerable development of tuffogeneous and coarse clastic formations in the upper parts of the Albian and in the Cenomanian; whereas the base of the Turonian is represented by rather conspicuous silico-calcareous rocks of the Ananaur

horizon, characterized by the presence of *Radiolaria*. The Upper Turonian is represented in both regions by red limestones and marls with single bands of tuffs, while the Orbitoidal (Maastricht) beds are transgressively overlying older formations. The foregoing supports the contention that the Lagich mountains and the Kakhetia range have one common geotectonic zone and one cordillera, which had ranged from the Jurassic up to the Oligocene according to one common plan.

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Received
5. XI. 1938.

REFERENCES

[1] К. И. Богданович, Тр. Геол. ком., нов. сер., вып. 26 (1906). [2] N. B. Vassoevich, C. R. Acad. Sci. URSS, XXI, No 3 (1938). [3] Отчет о деятельности Нефт. геол.-разв. ин-та за 1935 (1936). [4] В. Е. Хаин, Геологич. исследов. и поиски нефти в Лагичских горах (1937).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

STRATIGRAPHY

ON THE PRESENCE OF ALBIAN DEPOSITS IN NORTH-EASTERN AZERBAIDJAN

By N. B. VASSOEVICH

(Communicated by A. A. Borissiak, Member of the Academy, 10. XI. 1938)

The history of differentiation of the Aptian, Albian and Cenomanian in the section of Cretaceous deposits of the south-eastern terminus of the Main Caucasus Range is closely connected with the revision of the age of the «Actinocamaxian» horizon and the «Orbitoidal series», established by K. I. Bogdanovich during his route explorations in the Dibrar system in 1902 and 1904. In the monograph published in 1906, Bogdanovich referred the «Actinocamaxian» horizon, composed by «reddish and grey, sometimes variegated, marly clays and subordinate bands of marls and calcareous sandstones», to the base of Senonian and upper parts of Turonian. This was based on the occurrence in the aforesaid beds of belemnites, designated by K. I. Bogdanovich as *Actinocamax plenus* Blainv. mut. *caucasicus* Bogd.

Two years later, in 1908, E. Stolley reexamined the belemnites from the collection of K. I. Bogdanovich and determined the age of the surrounding strata as Aptian and Lower Albian. He allocated part of the «actinocamaxes» to *Neohibolites ewaldi* Stromb., and part (var. α)—to *N. strombecki* Müll. The former occurs in Germany in the zone of *Parahoplites deshayesi* Leym., i. e. in the upper zone of the Lower Aptian (after Koenen and Kilyan); *Neohibolites strombecki* Müll. are widespread in the North German Lower Albian (zone *Leymeriella tardefurcata* Leym.).

In 1935 Z. A. Mishunina had found that *Parahibolites (Neohibolites) strombecki* Müll. are distributed, in association with *Parahibolites ewaldi* Stromb. and other Aptian forms, throughout the entire section of the middle and lower parts of the red-coloured «Actinocamaxian» series. It would seem that that had invalidated the contention of E. Stolley about the allocation of a part of «Actinocamaxian» layers to the Albian.

Further explorations in north Kabristan have led to the location of *Neohibolites stylioides* Renng. in beds overlying the «Actinocamaxian» horizon, which suggested the presence of the Upper Albian in this part of south-eastern Caucasus. The Middle and Lower division of Albian remained unknown, and the corresponding place in stratigraphic schemes was filled in by «break» (see the table). Numerous investigators had believed that there were no Albian deposits whatever in the Dibrar system and in the adjoining regions (M. F. Mirchink, S. F. Fedorov, I. M. Goubkin, P. P. Avdusin, M. A. Glessner and others).

The new data, derived by us in the fall of 1937 and at the beginning of 1938, have furnished substantial evidence in favour of the existence of Albian deposits both in the Dibrar Flysch zone and the Cis-caspian, zone Shakh-dag-Atachaisk. We succeeded in establishing the exact age of separate hori-

zons, owing to the determination of the fauna we had collected by G. J. Krymholtz and T. Mordvilko.

The most curious, though incomplete section of Albian deposits was observed in the district of the Kilyaz station, on the southern limb of the Zorat syncline. That was exactly where fauna was gathered allowing to determine with more precision the age of single horizons of the Albian. The terrace shelf near the station Kilyaz shows how immediately above the bed-pack of red, often calcareous clays, containing poorly preserved *Neohibolites* (*N.* ex gr. *ewaldi* Stromb.?), are resting red unstratified and uncalcareous clays with intercalations of light keffekelite (the upper parts of the Khanagin and lower parts of the Alty-agach series), followed by younger strata of the Alty-agach series:

1. Multicoloured (green, olive, brown, grey and black) uncalcareous clays, interbedded with lighter soft marls, middle and coarse-grained calcareous sandstones, growing brown in weathering. Sparse intercalations of keffekelites («ghyl-abi»). Single clay bands contain along fissures great quantities of gypsum and yellow iron-sulphates. A noteworthy feature is the presence of neptunic sandy dykes, which are very characteristic of the naphtiskhevi of eastern Georgia. The upper horizons of the multicoloured pack abound in *Neohibolites minor* Stolley (definition of Krymholtz). Thickness—25 m.

2. Light-coloured (whitish, straw-coloured and greenish-grey) marls and marly limestones with intercalations (a few cm thick) of middle and coarse-grained slightly calcareous and calciferous sandstones, bearing prismoid shells *Inoceramus* and *Foraminifera* (*Lenticulina* and others). Occasionally occur *Neohibolites minimus* List. (designated by Krymholtz). Thickness 5 m.

3. Marls with interbedded, for the most part non-calcareous clays and sandstones. The basal parts of the pack contain greater quantities of marls, while in the upper parts clays are prevailing. Thickness—2.5 m.

4. Grey and olive-green uncalcareous clays, skirting the section of the Alty-agach series. Thickness—2 m.

Interval. Thickness—several metres.

5. Fine-grained quartz-feldspathic, somewhat tuffogeneous sandstones (layers up to 1 m in thickness), separated by greenish uncalcareous clays, with alternating streaks of argillites and ghyl-abi (up to 18 cm). In the topmost parts of this bed-pack, corresponding to the lower division of the Cululine series, have been observed *Aucellina* and in thin-sections—calcified *Radiolaria*. Thickness—about 10 m.

6. Marls with alternating bands of clays, argillites and calcareous sandstones. The basal parts contain two bands of ghyl-abi (approximately 10 cm each). Throughout the entire bed-pack are widespread *Aucellina gryphaeoides* Sow. (according to the definition of Mordvilko). Fish remains are of less frequent occurrence. In the uppermost parts of this «Aucelline» horizon *Neohibolites* sp. have also been met. Thickness—about 5 m.

7. Olive, greenish and sometimes dark-grey, usually calcareous clays with intercalations of marls, argillaceous sandstones, argillites and ghyl-abi. The above are already marking the base of the Kemshidag series. Thickness—2.35 m.

8. Olive, greenish and brown clays, practically always of the loam type and non-calcareous. Sparsely interbedded with argillites and alevrites. There are a few interlayers of ghyl-abi (in the roof of the bed-pack is resting a layer 18 m thick). Not infrequently the rocks contain *Radiolaria*. Thickness—2.6 m.

9. Pack of the foregoing type, but containing interbeds of reddish calcareous clays and thin streaks of marl. There have been encountered *Neohibolites* cf. *ultimus* d'Orb. and *N. subtilis* Krymh. Thickness—0.65 m.

K. I. Bogdanovich, 1906	N. S. Shatsky, 1930—1931	Interpretation of the section by N. B. Vassoevich		M. F. Mirchink, 1931	Z. A. Mishunina, 1932	Z. A. Mishunina, 1935
Horizon *a* of Orbitoidal series—Upper Senonian	Orbitoidal strata	Kemchi series		Kemchi series	Orbitoidal strata (Maastricht)	Kemchi series. Coniacian stage and Upper Turonian*
	Break			Emscher		
	Bed-pack *a*—grey marls, red clays and bituminous shales Bed-pack *b*—marls and limestones	(no break) occasional discontinuity		Kemish-dag series	Break and unconformability of dip	Break Sub-Kemchi series: 3. Clays with intercalations of sandstones Cenomanian
	Bed-pack *c*—dark grey clays with interbeds of marls containing fish remains. Analogue of Middle and Upper Albian deposits of Daghestan	Kemish-dag series	Cenomanian-Turonian	Cululine series		Upper Albian: 2. Marls with interbedded clays and sandstones 1. Sandstones with bands of clays
	Thick series (?) of grey and greenish-grey clays with intercalations of sandstones attaining 2—2.5 m in thickness at the base	(Cenomanian)			Sub-orditoidal strata Albian	
		Cululine series (Upper Albian)		Unconformity and break		Break
Occasional unconformity						
Break?	Red-coloured rocks with belemnites	Khanagin series		Khanagin series. Upper parts of Aptian	Series of red clays. Aptian	Red-coloured series Upper Aptian
Actinocamaxian horizon (basal parts of Senonian and upper parts of Turonian)						

* Another scheme, also published in 1935, shows only Upper Turonian.

M. F. Mirchink, 1935	V. E. Khain, 1937	S. F. Fedorov, P. P. Avdusin, M. A. Giessner and others, 1937	I. M. Goubkin, S. F. Fedorov, 1938		N. B. Vassoevich, 1937—1938
Kemchi series. Coniacian stage, possibly base of Santonian	Kemchi series. Lowermost parts of Santonian-Coniacian stage	Kemchi series. Emscher-Upper Turonian	Kemchi series	Emscher	Carbonaceous Flysch series of Kemchi-Dibrar zone=Khigin conglomerate series of Atachai zone (Analogue of the lower part of series Ekhmakis-khevi and horizons Margalitis-kide and Ananur. Coniacian and Turonian)
Break and unconformity	Upper Turonian / Break	Break	Break	Turonian	
Sub-Kemchi series-Cenomanian (?): Clays with interbeds of sandstones	Sub-Kemchi series (Lower Turonian, Cenomanian and Upper Albian)	Sub-Kemchi series	Sub-Kemchi series		Occasional discontinuity: Kemishdag series / Analogue of the Ukugmarti of Kakhetia and South Ossetia series
Sandstones and marls					Cenomanian
Sandstones		Upper Cenomanian	Cenomanian		Analogue of the Naphtis-khevi series of Kakhetia and South Ossetia: Argillites, marls, siltstones, clays and microconglomerates with *Neohibolites stylioides* Renng and *Aucellina gryphaeoides* Sow. Vrakonian stage — Upper division of Cululine series K_1; Sandstones and clays with agglutinated *Foraminifera* and calcified *Radiolaria* — Lower division K_1
Break (dip to the Albian)	? (unconformity and break)	Break (dipping to the Albian and Lower Cenomanian)	Break (Albian)		Occasional unconformity: Alty-agach series: Tankalacian horizon — marls with *Neohibolites minimus* List.; Middle Albian / Clays with *Neohibolites minor* Stolley. Upper parts of Lower Albian / Variegated clays of the Clanseian
Upper half of Aptian	Series of red clays. Upper Aptian	Aptian	Aptian		Khanagin series (s. str.). Analogue of upper strata of tetra-khevi series of Kakhetia. Aptian

The strata in the given section refer to the Lower Albian, for their upper parts have yielded *Neohibolites minor* Stolley, characteristic of the upper portion of the zone with *Leym. tardefurcata*. Strata 2 correspond to the Dentate zone, and 5 and 6—to the Vrakonian stage, and ultimately, strata 9 belong to the Lower Cenomanian.

In the Flysch (Dibrar) zone at a number of localities there are observable unbroken sections of deposits, ranging from the Aptian up to and inclusive the Cenomanian, without traces of any appreciable intervals whatever.

Thus, at the upper course of the Pirsagat river the following section has been registered (from the base upward):

1. Grey shales with intercalations of siltstones (Khal-chai series).

2. Interstratified brown-ruddy and dark-greenish shaly, mostly calcareous clays, with intercalations of marls and siltstones. Single interlayers are enriched with manganeze oxide. There occur Aptian forms of belemnites. This is strictly speaking the Khanagin series. Thickness—about 75 m.

3. Alternating bands of dark-grey, greenish and to a less extent brownish-ruddy uncalcareous clays with interbeds of siltstones (lower subdivision of Alty-agach series). Thickness—12 m.

4. Beds similar to 3, except for the prevalence of reddish clays. This is the middle subdivision of the Alty-agach series. Thickness—25—30 m.

5a. Bed-pack of grey clays with interbeds of keffekelites. Thickness—4—5 m.

5b. Bed similar to 3, except for the prevalence of red clays at the bottom and at the top of the pack, and with alternating reddish and greenish clays in the centre (upper subdivision of the Alty-agach series). Thickness—20 m.

6. Bed-pack of siltstones with interbeds of reddish and greenish uncalcareous shales; the lower bed of siltstones has a thickness of 1.2 m. This is the lower subdivision of the Cululine series (Cululine sandstones). Thickness—6.5 m.

Higher up are lying, variegated by composition and colouring, rocks of the Aucelline horizon (the upper subdivision of the Cululine series). Thickness exceeding 20 m. This section strikes well against the section on the southern slope of the mount Dibrar, as well as the section along the Chikil-chai river, described by Z. A. Mishunina. The deposits developed at this place (Alty-agach series) and superimposed upon those analogous with bed-pack 2 of the section along the Pirsagat river, have been assigned by Mishunina to the Aptian, though no fauna has been revealed therein. The thickness of the Alty-agach series along the Chikil-chai river is in excess of 90 m, of which 20—25 m are referable to the lower subdivision, and about 35 m—to the middle one.

The upper subdivision of the Alty-agach series of the Dibrar zone is easily comparable to those layers of the Shakhdag-Atachai zone, which at that place contain Lower Albian *Neohibolites minor* Stolley. The Upper Albian bed-pack of Cululine siltstones and the overlying variegated rocks of the Aucelline horizon are traceable all over. A perfectly gradual transition between deposits of Alty-agach and Khanagin (s. str.) series leaves no ground for questioning the presence of the Clanseian stage in the section of the Aptian-Albian beds.

In general, unbroken sections ranging from the Tithonian to the Danian stage, and even up to the Lower Oligocene, in spite of the views which have been current until recent time, are not merely observable in a number of regions of the Dibrar Flysch zone, but constitute a typical feature of the latter.

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of Azerbaidjan. Baku.

Received
10. XI. 1938.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

EXPERIMENTAL MORPHOLOGY

THE ACTION OF AN EXCESS OF Na, K, Ca-CHLORIDES ON THE CYTOPLASMIC STRUCTURE OF EMBRYONIC TISSUE

By A. RUMYANTZEW

(Communicated by I. I. Schmalhausen, Member of the Academy, 11. XI. 1938)

In an earlier report (1) we have found that excess of any kind of chloride differently affects cells growing in vitro: $CaCl_2$ induces a compression of the protoplasm, which leads to a 40% loss in size of the nuclei, while KCl provokes a rapid vacuolization of the protoplasm and swelling of the chondriome. A similar tendency towards vacuolization and swelling is observed also in the case of an excess of NaCl.

We regarded the vacuolization of cells as the result of swelling, and the compression of protoplasm as a process of its inspissation. This assumption needed verification. Since the alterations arising in the cellular structures during the swelling and unswelling of protoplasm have been ascertained with some precision, in particular by the author (2), we decided to study these alterations as they arise in our experiments. Material: bits of tissue of the myocardium of a 6—8 day old chicken embryo. Media: I series—one drop of the chloride solution under test+the smallest possible drop of plasm; II series—1 part of plasm+2 parts of the solution under test. The tissue cultures were grown on slides and examined after 2—3 days in passing light or in the dark field. Intravital staining with neutral red (NR) or Janus green (JG). The total number of cultures studied in each series equalized 250, of which 50 were controls.

The first series of cultures supplied us with indications as to the specifity of the effect and thus supplemented the second, or the main experimental series. In the first series the tissue grew practically in a liquid medium. In the presence of KCl and $CaCl_2$ the growth was very scanty, more or less considerable zones of growth being observed only with NaCl. All the cultures degenerated in a short time. We were able to notice the following alterations.

NaCl. Growth spreading on the slide. The zone of growth is composed by flattened out cells. Their protoplasm is transparent, the fat droplets small and their number is less, than in the controls. The shape of the cells is in some polygonal, in others rounded, in the others again elongated. The protoplasm becomes vacuolized already in the course of the first day. On the second day almost every cell is vacuolized and manifests evident signs that it is dying. The chondriosomes have a typical, i. e. band-like, appearance on the first day, while on the second day they are represented by rounded formations or have the shape of thick rods. Intravital staining is quickly achieved. On the second day NR staining gives rise to granules

of 2 types: fine ones with caps, and larger ones staining allover an orange tint. These larger granules are vacuoles which were visible also without staining. In the dark field the protoplasm appears optically empty. Prolonged staining produces no great amount of new granulation. On the second day there appear alterations in the nuclei of the cells. These alterations consist in the loss of a regular shape and in the arising of small brilliant blocks.

In cultures of the 2nd series vacuolization appeared only on the second day. The vacuoles were usually small. The chondriosomes of the vacuolized cells showed alterations. The vacuoles and granules stained with NR similarly to those in the 1st series, but the amount ot granulation was always less than in the controls. No alterations were observed in the nuclei. In some cases the growing cells formed—as the result of the fusion of their ectoplasm—a continuous membrane. Thus, so far as the character and the trend of the alterations were the same in both series, we are free to assume that the alterations which arise in cytoplasmic structures in the case of an excess of NaCl are the same as in that of swelling.

KCl. Series I. Most of the cells emerging into the medium possess no stellar shape, neither do they show any process. They are either round or polygonal, their protoplasm is visibly vacuolized. On the second day and sometimes already on the first isolated cells unite and form large vacuolized layers with altered nuclei. Sometimes, however, these layers fail to form, but the protoplasm of the cells spread out on the slide is always greatly vacuolized, the vacuoles reaching the size of the nucleus, as this has been also observed by Möllendorf ([3]). After staining such cultures it can be established that the chondriome is represented by thick rods and round swollen granules. NR-granulations are few, but the vacuoles of the protoplasm are intensely stained, the stain deposited in them acquiring an orange-red tint. No new granules or vacuoles are formed if the action of NR is prolonged, only the stain regularly flocculates in the vacuoles. In the dark field the protoplasm is optically empty and displays an intense motion of fat particles: the latter are not numerous and very fine.

Similar alterations, though not so marked, are observed in the second series. On the second day the protoplasm of most cells is vacuolized and there is a tendency towards the formation of acellular layer. The protoplasm is optically empty and liquified; the Brownian motion of fat particles is well visible. The chondriome is altered and increases in size, but does not form such clods and swollen blocks as in series I. After prolonged staining with NR there appear no additional stained granules in the strongly vacuolized cells. All this considered together suggests that in KCl as well there is a considerable hydration of the protoplasm; it is expressed in a great increase of the hydrous phases, and this results in the arising of vacuoles of considerable size.

$CaCl_2$. Growth always scanty. In the small growth zone of the culture of series I, if it does form, one sees almost no flattened polygonal cells. The cells are usually elongated or angular and are always supplied with thin processi. Among the angular cells one encounters smaller ones with short branching processi; the fat droplets in the protoplasm are always small. A fine vacuolization is sometimes noticeable in the protoplasm of the cells; at the borders of the growth zone compressed rounded cells are observed; they are small and show evident signs of degeneration. After staining with NR and JG it is easy to see, that NR accumulates in the form of fine granules in the endoplasm; their number increases after prolonged staining, but their size remains unchanged. The chondriosomes have the shape of fine granules or of thin rods; band-like chondriosomes, similar to those in normal cultures or in cultures with NaCl, are extremely scarce. In the dark field the proto-

plasm shines a milky, dull light; there is no Brownian motion, nor any flowing motions of the protoplasm.

In the second series the cells are mostly spindle-shaped, or angular, though flattened out cells are also encountered. The cells are linked by thin processi. The chondriosomes are almost normal. The fat droplets are fine. The numerous NR-granulations are fine and have an evident tendency towards increasing under a prolonged action of the stain. Such alteration, particularly if one takes into account the decrease of the cell size described earlier (1), obviously point to a dehydration of the protoplasm, which sets in in the case of an excess of $CaCl_2$ in the medium. On the second day there are many degenerating cells at the border of the zone of growth.

Comparing the results obtained with what was already known concerning the action of cations on protoplasm, we arrive at the conclusion that our observations are in good agreement with the views of Spek (4), Chambers (5), Fouré-Fremiet (6), Gellhorn (7) et al., who affirm that Na and K provoke liquefaction, while Ca leads to an inspissation of the protoplasm. It would be added that the above effect is observed not only when these cations are tested separately, but also when one of them is in excess, as this was the case in our experiments. Moreover, after the works by Spek (8), Chambers-Reznikoff (5), Lepeschkin (9) et al. it can be considered, that turbidity of the protoplasm is an indication of beginning coagulation under the influence of salt penetrating into the protoplasm. In $CaCl_2$ (ser. I) turbidity was observed already in the course of the first 24 hours, while in NaCl (ser. I) only after the cells began to die off, i. e. on the 2nd or 3rd day. Vacuolization of the protoplasm was observed in every case. This points to the fact that Na, K and Ca act not only on the surface of the cells, but penetrate into them. We know very little of the mechanism of the action of the penetrating cations on the particles of protoplasm, yet we can affirm that different cations affect them in a different way.

The difference in the staining with NR and in deposition (rapid staining in KCl and NaCl and a slower one in $CaCl_2$) and the inability to form new granules (Krinom according to Khlopin) (in KCl and NaCl contrary to $CaCl_2$) suffice to show that the condition of the protoplasm is different in these cases and its permeability is not the same.

Without attempting to analyze these conditions of the protoplasm, we decided to examine the only question, accessible to our investigation, i. e. whether the observed phenomena of demixing and coagulation are reversible or they are a sign of beginning irreversible degeneration. To solve this question we cut the bits of tissue, typically altered by the action of the salt under test, into pieces on the 3rd day of cultivation and transferred them into a fresh portion of the normal medium (1 part of plasm+1 part of embryonic extract). After 24 hours we already could observe in the zone of growth healthy cells, differing in nothing from those of the control cultures. No great quantity of cell debris or of evidently degenerating cells was to be seen on the 2nd day neither. This seems to show the complete reversibility of such phenomena as vacuolization of the protoplasm, swelling and partial disruption of the chondriome, arising of fine granularity, etc. Only in the subcultures of those tissue cultures, in which we observed the formation of layers (cultures in KCl) or in which the nuclei of the cells acquired an angular or irregular shape, there was no growth, i. e. the protoplasm in these cases had suffered irreversible alterations.

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Received
11. XI. 1938.

REFERENCES

[1] Rumyantzew, C. R. Acad. Sci. URSS, XX, No 7—8 (1938). [2] Румянцев, Арх. анат. гист., VII, 11 (1928). [3] Möllendorf, Zeit. f. Zellforsch., **23** 745 (1936). [4] Spek, Act. Zool., **165** (1921). [5] Chambers a. Reznikoff. Journ. Gen. Phys., 8, 369 (1926). [6] Fouré-Fremiet, Protoplasma, **6**, 521 (1929). [7] Gellhorn, Das Permeabilitätsproblem (1929). [8] Spek, Arch. f. Protist., **46**, 166 (1925); Protoplasma, **4**, 321 (1928). [9] Lepeschkin, Protoplasma, 2. 239 (1927); Kolloid. d. Protoplasmas (1938).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XXI, № 8

PALEONTOLOGY

HORIZON WITH *CONGERIA SUBRHOMBOIDEA* ANDRUS. IN THE KUBAN PROVINCE

By A. G. EBERZIN

(Communicated by A. A. Borissiak, Member of the Academy, 11. XI. 1938)

«Strata, containing *Congeria subrhomboidea*, have attained marked development in the Kuban province. The authors ([2]—[5]) believe that the range of vertical distribution of the latter form is more considerable here, than on the Kerch and Taman peninsula. I certainly agree that it exhibits here far greater thickness, as its presence is apparently due to littoral sediments, which over there are represented merely by thin interbeds. The argillaceous horizon VI*, the arenaceous IV and the Valenciennese clays replacing the latter are grading into detrital limestones in the coastal regions of the Kuban province, and therefore the occurrence of the aforementioned form in strata, equivalent to horizon VI, V and probably even IV (possibly III) is a matter of course; it seems doubtful, however, that it should occur stratigraphically any higher. Neither do I know, whether it is to be found in the lowermost (so to speak, the most typically Odessa) horizon of the Kuban province.

At any rate, most frequently here are met limestones (mostly detrital) and shell deposits with fauna closely related to the one of horizon V, for very often the leading congeries are listed in association with Odessa elements *(Parvivenus widhalmi)*, but these shell limestones, naturally, correspond not just to V, but at any rate to IV, V and VI together». The above is a quotation from a treatise by N. I. Andrusov on the Pontian stage, published in 1917 [(1), pp. 15—16].

In the summer of 1938, during paleontological explorations in the Krasnodar region, I had the opportunity of visiting some localities with Pontian deposits and observing the correlation between the horizon with *Congeria subrhomboidea* Andrus. and adjacent beds. New data derived from these investigations have contributed to a clearer understanding of the views held on the stratigraphic position of the horizon with *Congeria subrhomboidea* Andrus. in the Kuban province, and to answer some of the questions raised by N. I. Andrusov.

* Roman figures III—VI, after the system of N. I. Andrusov, denote stratigraphic horizons of the classical Kamysh-burun exposure of Pontian deposits (Kerch peninsula). In ascending order, from the base upwards, the horizons follow one upon another thus: horizon VI—schistous clays with minute *Paradacna abichi* R. Hörn. (Lower Valenciennese clays); horizon V—brittle limestone with *Congeria subrhomboidea* Andrus., horizon IV—argillaceous sandstones containing *Didacna incerta* Desh. var. *fragilis* Andrus. and horizon III—cross-bedded faluns with *Congeria subcarinata* Desh.

In this respect, abundant material has been furnished by the section of the Lower Pontian quarried on the right slope of the «crevice» (ravine) Krutenko in the district of Ilsk.

Upon dark (nearly black in fresh fracture) paleogene clays, with ocher-yellow spots and streaks of bituminous sand, there are discordantly lying thick-bedded series of limestone-shell deposits up to 20 m in thickness, dipping northward (As. 5° NO) at an angle of 20°.

The lower strata show a prevalence of shell-limestones, in places arenaceous, with lenticular sand-streaks. These shell-limestones are grading upward into yellowish and brownish conchoidal limestones, porous, and in the upper portion of the series markedly recrystallized and consolidated. Fauna in a good state of preservation occurs in the lower beds, wherein it is represented by the following species: *Congeria novorossica* Sinz., *C. galisgensis* Andrus., *C.* sp. ex gr. *subcarinata* Desh., *Dreissensia* cf. *tennuissima* Sinz., *Dr.* cf. *simplex* Barb., *Dr.* aff. *stefanescui* Font., *Didacna* cf. *novorossica* Barb., *Monodacna pseudocatillus* Barb., *M.* sp., *Prosodacna littoralis* Eichw., *Pr. littoralis* Eichw. var. *orientalis* Andrus., *Pr. barboti* Andrus., *Pr. eichwaldi* Andrus., *Parvivenus widhalmi* Sinz., *Neritina* cf. *pseudodanubialis* Sinz., *N.* sp., *Melanopsis* gr. *esperi* Fer., *M.* sp., *M. (Lyrcea)* sp., *Lithoglyphus* cf. *neumayri* Sinz. etc. Higher up these species are associated with larger sized shells of *Didacna*, *Didacnomya* (?) and *Plagiodacna* aff. *carinata* Desh., but in general the character of the fauna remains unchanged.

The occurrence in the described limestone beds of *Congeria novorossica* Sinz., *Monodacna pseudocatillus* Barb., *Prosodacna littoralis* Eichw., *Parvivenus widhalmi* Sinz., and other forms, confined to the Odessa limestone, qualifies the age of the limestone series as Lower Pontian. It is noteworthy that while bearing great resemblance faunistically and partly lithologically with the Odessa limestone, the Lower Pontian deposits of the Ilsk district are at the same time very similar to the Lower Pontian beds of the Odessa type of the Stavropol district. The following species are common and peculiar to both districts: *Congeria galisgensis* Andrus., *Prosodacna eichwaldi* Andrus., *Pr. barboti* Andrus. and others.

No matter how carefully I was searching for shells of *Congeria subrhomboidea* Andrus. in the Lower Pontian shell-deposits and limestones of the Ilsk district, I failed to locate there the aforementioned species. Therefore the question of N. I. Andrusov «whether it is to be found in the lowermost (so to speak, the most typically Odessa) horizon of the Kuban province» should be answered in the negative.

What is the correlation between the horizon with *Congeria subrhomboidea* Andrus. and the horizon with the Odessa limestone? The answer to this question is provided by the upper portion of the section of the Lower Pontian at the Krutenko ravine. Over here, immediately above the aforesaid limestone-beds, are lying conformably and in unbroken continuity bluish-grey, strongly argillaceous sands with brownish sand-streaks, bearing fauna as follows: *Congeria subrhomboidea* Andrus., *Didacna* sp. (gr. *novorossica-incerta*), *Limnocardium subsquamulosum* Andrus., etc. Visible thickness—about 3 m.

Thus, the given section testifies that the horizon with *Congeria subrhomboidea* Andrus. is overlying the Lower Pontian deposits, represented in the facies of the Odessa limestones.

Inasmuch as the works of N. I. Andrusov have proved the Lower Valenciennese clays and the Odessa limestones to be synchronous, it may be deduced therefrom, that the horizon containing *Congeria subrhomboidea*

Andrus. (as far as its lower limit is concerned) is resting in the Kuban province at the same stratigraphic level, as on the Kerch and Taman peninsula and in western Transcaucasia.

In addition to the Krutenko ravine, outcrops of the horizon with *Congeria subrhomboidea* Andrus. in the Ilsk district are observed at the ravines Kuznetzova, Gnilaya, Denisenko (Karskaya) and Kulinskaya. Unfortunately, owing to poor exposure and to scattered outcroppings, it has been impossible to see its direct relation to the adjacent horizons, though it may be noted that in this region the aforesaid horizon lies stratigraphically appreciably lower than horizon III Kamysh-burun, is independent and separated from the latter by a stratigraphic interruption, not less than 20 m in thickness.

Due to inadequate exposure, it has been impossible to determine the actual thickness of the horizon with *Congeria subrhomboidea* Andrus. Eastward of the Ilsk district, along the Shebsh river bank, the visible thickness of this horizon attains 10 m. Whether this is the real thickness, or somewhat underestimated, is difficult to judge, the exposure being of unreliable quality.

Now remains the question as to what correlation exists between the horizon with *Congeria subrhomboidea* Andrus. and the horizon IV Kamysh-burun.

An excellent exposure of the latter has been observed by me in the region of Kaluga oil-fields on the left bank of the Ilitch river, along the right edge of the ravine Kamyshevaya. A thick series (up to 15 m) crops out there, made up of brownish-grey fine-grained slightly argillaceous sands, with subordinate streaks of thin-bedded bluish-grey arenaceous clays, observable also at the base of the sands. The following faunal species have been recorded there: *Dreissensia anisoconcha* Andrus., *Dr. anisoconcha* Andrus. var. *kitenica* Andrus., *Dr. rostriformis* Desh., *Dreissensiomya aperta* Desh., *Didacna incerta* Desh. var. *fragilis* Andrus., *D.* cf. *sulcatina* Desh., *Didacnomya corbuloides* Desh., *Kaladacna steindachneri* Brus., *Limnocardium subsquamulosum* Andrus., *L. subsyrmiense* Andrus., *Monodacna subdentata* Desh., *Phyllicardium planum* Desh., *Paradacna abichi* R. Hörn., *P. retovskii* Andrus., *Prosodacna semisulcata* Rouss., *Pr.* gr. *rumana* Font., *Pr.* n. sp., *Plagiodacna carinata* Desh., *Valenciennesia* sp., *Planorbis* sp. Like at Kamysh-burun, this is a case of mixed faunas from Valenciennese clays with faluns.

The sands described above are gently dipping northward. Their basal parts are cropping out at the subjacent (southward) ravine, where a succeeding section is manifest. Below the vegetative and soil covering there follow in downward succession:

1. Bluish-grey arenaceous clays with alternating yellowish-brown bands, containing vegetative remains and fauna: *Dreissensia anisoconcha* Andrus., *Didacna incerta* Desh. var. *fragilis* Andrus., *Prosodacna* gr. *rumana* Font. etc. Visible thickness—0.35 m.

2. Consolidated coarse-grained sands, their upper parts rust, coloured with a bluish tint, with fine well-rounded quartz pebbles and coloured flint, with shell detritus, wherein the following forms have been registered: *Congeria subrhomboidea* Andrus., *Dreissensia rostriformis* Desh. var. *minor* Andrus., *Dr. angusta* Rouss. var. *minor* Andrus., *Dr.* cf. *stefanescui* Font., *Kaladacna steindachneri* Brus., *Limnocardium subsquamulosum* Andrus., *Monodacna* ex gr. *pseudocatillus* Barb., *Phyllicardium planum* Desh., *Plagiodacna carinata* Desh., *Prosodacna* cf. *littoralis* Eichw. Visible thickness—0.50 m.

3. Thick beds of bluish-grey clays with *Congeria subrhomboidea* Andrus.,

Limnocardium subsquamulosum Andrus., *Valenciennesia* sp. Visible thickness—0.75 m.

4. Greenish-grey, fine-grained detrital sands with *Congeria subrhomboidea* Andrus., *Dreissensia anisoconcha* Andrus., *Dr. rostriformis* Desh. var. *minor* Andrus., *Dr.* cf. *stefanescui* Font., *Neritina* sp. Visible thickness—0.15 m.

5. A thin bed of fine-shelly arenaceous detritus with *Congeria subrhomboidea* Andrus., *C. subcarinata* Desh., *Prosodacna* sp., *Viviparus* sp. Visible thickness—0.10 m.

6. Blue arenaceous clays, olive-grey at the top, with thin interspersion of detritus, with rare *Congeria subrhomboidea* Andrus., *Paradacna* cf. *retovskii* Andrus. Visible thickness—0.30 m.

All of the above strata are gently dipping northward (As. 10° NO∠4°).

From the above section it is evident that the 1st layer pertaining to horizon IV Kamysh-burun is underlain by a series of sands and clays (layers 2—6) with visible thickness 1.8 m, which may be referred to the horizon with *Congeria subrhomboidea* Andrus.

Thus, in regard to the upper border of the subrhomboidal horizon, we have recognized the same phenomenon, which has been observable at all the other points of the Black Sea basin: conformably overlying the horizon with *Congeria subrhomboidea* are seen strata corresponding to horizon IV Kamysh-burun (base of the Upper Pontian—Bosporus substage).

In summing up the foregoing, it may be stated that the stratigraphical position of the subrhomboidal horizon, identified by N. I. Andrusov on the boundary between the Upper and the Lower (the top of the latter) divisions of the Pontian stage, is, according to my observations, manifest in the Kuban province as well.

A statement to the effect that *Congeria subrhomboidea* Andrus. occurs not only in this horizon, but in other horizons as well, i. e. that it has a far greater range of vertical distribution over here than in Kerch, Taman and other points, would not be warranted for lack of evidence.

The existing erroneous view as to the wide range of its vertical distribution throughout the Kuban province is due, perhaps, to the fact, that the subrhomboidal horizon attains here far greater thickness than elsewhere. Thus, in Kerch it is equal to 1.7 m, and along the Shebsh river the visible thickness is about 10 m.

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Received
11. XI. 1938.

REFERENCES

[1] Н. Андрусов, Геология России, IV (2), ч. II, вып. 2 (1917). [2] И. М. Губкин, Тр. Геол. ком., нов. сер., вып. 115 (1915). [3] К. А. Прокопов, там же, вып. 92 (1914). [4] К. А. Прокопов, там же, вып. 112 (1922). [5] С. И. Чарноцкий, там же, вып. 91 (1914).

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